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General Subjects

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry upon payment of the dues ($2.50) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Division of Rubber Chemistry upon payment of $5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $5.00 per year.

To these charges of $2.50 and $5.00, respectively, per year, extra postage must be added at the rate of $.20 per year for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio, or to the Office of Publication, 1500 Greenmount Ave., Baltimore, Maryland.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

HISTORY OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY *

E. V. Osberg

Associate Editor, India Rubber World

After long years of experience, the rubber industry of today has come to realize the true worth of the chemist and the value of the interchange of scientific knowledge and coöperation in research. Early meetings and discussions held by the Division of Rubber Chemistry of the American Chemical Society and its predecessor, the Rubber Section, were influential in dispelling early ideas as to the value of the chemist and in breaking down the barrier of secrecy in the rubber trade. The chemistry of rubber during the past two decades has undergone a tremendous growth, and the Division through its many activities has played an important role in disseminating knowledge that has been gained from laboratory research.

THE EARLY RUBBER CHEMIST

Before the turn of the twentieth century, the rubber industry had little or no knowledge of the chemist or what he might accomplish. Funds for research were generally withheld, with no quick profits in sight as a result of these expenditures. Among the comments of rubber manufacturers of that time were: "I have no use for chemists, druggists and apothecaries"; "I would give more for the guess of my old superintendent than all the certainties of the best chemist on earth"; "I had employed chemists but their cost to the company had been greater than any value received from their work."

In 1899 the chemist, Arthur H. Marks, invented the alkali reclaiming process, and in 1906 George Oenslager discovered organic accelerators. Rubber technology was being revolutionized by the chemist, and larger profits were in sight. The tight grip on the purse strings became loosened somewhat, and money was being cautiously expended on research. Practical and immediate results which could be translated into hasty profits were the principal aims. Little encouragement was afforded those who wanted to tackle fundamentals. Competition was keen among manufacturers; the rubber industry was growing rapidly, and no time or money was available for abstract reasoning or for "profitless" research enterprises.

Rubber manufacturers were quite willing for their chemists to meet with chemists of other companies provided they did not divulge any of the firm's "secrets". With most of those attending these early meetings in the role of listeners, little was accomplished in furthering the knowledge of rubber chemistry through the exchange of ideas. Such was the problem during the life of the Rubber Section and through the earlier years of its healthier successor, the Division of Rubber Chemistry.

THE AMERICAN CHEMICAL SOCIETY—1876

The parent organization, the American Chemical Society, had its inception in the summer of 1874, when a representative group of chemists met at Northumber-

* Reprinted with certain modifications from the *India Rubber World*, Vol. 101, No. 1, pages 83-88, October 1, 1939.

land, Pa., to celebrate the centennial of the discovery of oxygen by Dr. Joseph Priestley and other notable discoveries of the year 1774. This meeting resulted in the formation of a subsection of chemistry in the American Association for the Advancement of Science. Many progressive chemists of the day, however, were not satisfied and wanted a completely independent organization. To further this aim, a meeting was held on January 27, 1876, in the New York City home of Professor C. F. Chandler of Columbia University, and a committee was named to attend to the preliminaries of organization.

The organization meeting was held April 6, 1876, at the College of Pharmacy in New York. John W. Draper was elected first president of the new society; W. M. Habirshaw, well-known throughout the rubber trade of that time, was made treasurer. The first membership list contained the names of 53 resident (New York City) and 80 non-resident members, a total of 133. The first regular meeting after organization was held May 4, 1876, and by December of that year the membership had grown to a total of 230, and in 1901, twenty-five years after its origin, the society boasted of a membership of 1,809. In 1939, the society membership rolls numbered 23,300.

On November 9, 1877, the American Chemical Society was legally incorporated under the laws of the State of New York, the incorporation being adopted by the Society at its meeting on December 6, 1877. After a steady growth of sixty years under the New York charter, the society was reëncorporated on January 1, 1938, under federal laws. Through the adoption of the national charter, which became available through an act of Congress, the Society now legally conforms to its national scope.

PURPOSE OF THE AMERICAN CHEMICAL SOCIETY

During its sixty-three years of existence the American Chemical Society has striven for the following objects: the advancement of chemistry in all of its branches; the promotion of research in chemical science and industry; the improvement of the qualifications and usefulness of chemists through high standards of professional ethics, education, and attainments; the increase and diffusion of chemical knowledge; the promotion of scientific interests, education, and inquiry, and the development of our industries by chemical aid. The objects of its branches are the same as those of the society. The Division of Rubber Chemistry has gone far on this road of progress, despite the handicaps encountered during the period extending from the time of its inception to that of general acceptance by the industry.

RUBBER CHEMISTRY SECTION OF THE AMERICAN CHEMICAL SOCIETY—1909

Predecessor of the Division of Rubber Chemistry was the India Rubber Chemistry Section, later known as the Rubber Chemistry Section. Organization was effected on December 30, 1909, at a meeting of the American Chemical Society in Boston, Mass. The purpose set forth by this enterprising group of 28 men, present at the initial meeting, was to bring together at occasional meetings chemists and others interested in the field of rubber so that many problems of moment and interest could be solved by united effort. High hopes were held for the new Section, and it was generally anticipated that a regular division would be organized within a very short period.

The first chairman of the new Section was Charles C. Goodrich, and the first secretary, Frederick J. Maywald. Among the others actively associated with the

Section at its inception were: Edward A. Barrier, Milton E. MacDonald, William G. Hills, Sheldon P. Thatcher, W. C. Geer, G. Oenslager, Harvey M. Eddy, H. Hughes, Harold van der Linde, M. L. Allard, C. R. Boggs, C. E. Waters and G. H. Savage.

The high enthusiasm of the new enterprise soon died down when subsequent meetings were held without constructive results of any consequence. At this time chemical developments in the rubber industry were not generally protected by patents, and manufacturers were extremely careful to prevent disclosure of their processes and developments. This reticence naturally retarded the development of the Rubber Section. Early activities were limited chiefly to the standardization of methods of chemical analysis and physical tests of rubber articles. Mutual effort in this phase of activity, however, struck a snag when rubber companies refused to reveal their methods of analysis, even when this information was to be treated with confidence as to the source.

Conditions were so bad that the following statement* was issued in 1911: "The American Chemical Society is very anxious that those of its members interested in the chemistry of India rubber should have their problems considered and solved. The India Rubber Section has had two meetings, but there is not yet sufficient evidence of real coöperative effort among the rubber chemists to insure success. The methods of analysis of India rubber are in almost a chaotic condition. The usual specifications for rubber goods meet the approval only of those who make them. The general chemistry of India rubber is sadly in need of improvement.

"Only the chemists actively interested in the India rubber industry can hope to improve affairs and it is, accordingly, necessary that they should really get together without too many padlocks on their lips if results are to be accomplished. It is certainly true that there are secrets of the rubber trade which cannot be disclosed, nor is there any desire that they should be disclosed, but when certain firms decline even to allow their methods of analysis to be known, it would certainly seem that secrecy is carried too far. The Section can never become a success if every member goes to its meetings with no idea of his responsibilities toward helpfulness, but simply to learn from others, many of whom may be in a similar position."

In connection with the working out of standard methods of analysis, much credit must be given to the Joint Rubber Insulation Committee, a group of manufacturers and consumers of insulated wire, which was formed in 1911 and supplied much of the data on tests utilized by the Rubber Section.

The papers presented at the meetings of the Rubber Section dealt largely with analytical methods, although occasionally other subjects were discussed, paving the way for future divergence of topics in the days of the Division of Rubber Chemistry, its successor. At a meeting of the Section in December, 1911, the subject of synthetic rubber was brought up by D. A. Cutler, section chairman, who spoke of experiments on synthetic rubber from isoprene obtained from turpentine. At the same meeting F. E. Barrows gave a short talk on the formation of the rubber molecule.

Toward the end of the Section's decade of existence the fruits of its labor were becoming evident. Analytical and test procedures were being perfected, and discussions on other subjects were becoming more frequent and livelier. The World War and rapid growth of the automotive industry had spurred technical activity in the rubber industry.

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* *India Rubber World*, Sept., 1911, p. 496.

Meetings of the Section were usually held in conjunction with those of the American Chemical Society and, with the exception of the years 1910 and 1915, the Section met during each year of its existence. The following table presents a résumé of the Section's activities, its chairmen and its secretaries.

MEETINGS OF THE RUBBER CHEMISTRY SECTION, AMERICAN CHEMICAL SOCIETY

Date	Place	Attendance	Chairman	Secretary
Dec., 1909	Boston	28	Chas. C. Goodrich	F. J. Maywald
June, 1911	Indianapolis	16	Chas. C. Goodrich	F. J. Maywald
Dec., 1911	Washington	54	Chas. C. Goodrich	F. J. Maywald
Apr., 1912	New York	36	D. A. Cutler	D. Whipple
Mar., 1913	Milwaukee	—	D. A. Cutler	D. Whipple
Sept., 1913	Rochester	—	D. A. Cutler	D. Whipple
Apr., 1914	Cincinnati	—	D. A. Cutler	D. Whipple
Sept., 1916	New York	110	L. E. Weber	J. B. Tuttle
Sept., 1917	Cambridge	80	L. E. Weber	J. B. Tuttle
Sept., 1918	Cleveland	80	L. E. Weber	J. B. Tuttle

The following list of names, believed to be quite comprehensive, has been compiled from the records examined, in which mention was made of their helpful activities during the existence of the Rubber Section.

NAMES CONNECTED WITH THE RUBBER SECTION—1909-1919

W. A. Ducca	C. E. Waters	I. V. Stone
J. B. Tuttle	G. H. Savage	J. A. Schaeffer
D. A. Cutler	M. E. MacDonald	H. B. Rodman
D. Whipple	L. G. Wesson	N. G. Madge
C. C. Goodrich	P. H. Walker	W. H. Smith
F. J. Maywald	W. W. Evans	H. Fay
C. M. Knight	F. E. Barrows	J. Westesson
E. A. Barrier	E. W. Boughton	C. P. Fox
W. G. Hills	C. D. Young	W. E. Piper
W. C. Geer	E. H. Johnson	G. T. Cottle
S. P. Thatcher	H. S. Upton	A. D. Hopkins
G. Oenslager	L. J. Plumb	D. Spence
H. M. Eddy	D. F. Cranor	J. W. Schade
H. Hughes	R. B. Earle	T. L. Wormley
H. van der Linde	A. H. Smith	J. E. Weber
M. L. Allard	H. E. Simmons	L. Yurow
C. R. Boggs		O. H. Klein

Early in 1919 plans to make the Rubber Chemistry Section a division began taking shape. By-laws were being prepared to submit to the Council of the American Chemical Society at its next meeting. Members of the executive committee of the Section active in the formation of the Division were: J. B. Tuttle, Chairman, D. Spence, G. Oenslager, L. E. Weber, H. E. Simmons, L. H. Plumb and A. H. Smith.

THE DIVISION OF RUBBER CHEMISTRY—1919

Recognizing the efforts of American rubber chemists to promote a high standing of scientific attainment in their industry, the Council of the American Chemical Society, meeting at Buffalo, N. Y., on April 7, 1919, authorized the organization of the Division of Rubber Chemistry. With this recognition came the obligation on the part of rubber chemists to coöperate to the fullest extent in raising the standard of their work.

The newly formed Division of Rubber Chemistry consisted essentially of the same group of men active in the old Rubber Section. However, any action taken by the Rubber Section had not been official until approved by the parent society. The supervision of the Section was entirely in the hands of the president and secretary of the American Chemical Society. Now, however, the rubber chemists could have a permanent organization, with officers elected by themselves; they could enroll their own members and, in general, act as a permanent body.

Great optimism reigned among the leaders of the new enterprise, and it was generally felt that the ten-year old bogey of secrecy was at an end. The ban on research disclosures, however, had not ended, and the early life of the new Division was concerned with fighting for greater freedom and expression of thought, as well as with the promotion of research on the fundamentals of rubber chemistry and physics.

The first meeting of the Division of Rubber Chemistry was held in Philadelphia, Pa., in October, 1919, under the chairmanship of J. B. Tuttle, who was active in the old Rubber Chemistry Section and in the formation of the new Division. Records show that a series of papers of a high order of merit were presented at this initial meeting. At subsequent meetings of the Division, a marked tendency to "open up" was noticeable. Less and less secrecy was being maintained by the various companies regarding their research activities and their developments in rubber compounding. This trend was promoted by the influx of new technical men into the industry, and by the increased utilization of patents for protection of processes and chemicals. As this move gained favor, the meetings were attended with increased interest. Coöperation was at last being achieved; the members of the new Division felt that the time was ripe for further extension of research. At a meeting in New York in September, 1921, the Division expressed its sentiment for coöperation in research between different manufacturers and also between manufacturers and producers by addressing the following resolution to the Rubber Association of America.

"It is a recognized fact that there are certain fundamental principles of general interest to the rubber industry as a whole, which no single company should be expected to develop. Therefore it is the sense of the Rubber Division, A.C.S., numbering approximately 200 members from all leading companies, both large and small, . . . that a coöperative research laboratory be established under the auspices of the Rubber Association of America for furthering the investigation of such fundamental problems."

This plea for coöperative research went unheard, but we have heard it reëchoed recently when W. C. Geer, pioneer in the formation of the old Rubber Section, addressed the members of the New York Group of the Division of Rubber Chemistry on "Research Coöperation in the Rubber Industry" on October 15, 1937, sixteen years after the 1921 proposal. Today, thirty years after the foundation of the Rubber Section, the challenge still remains; the solution of this problem may have an important bearing on the destiny of the rubber industry of the future.

The years passed, and the Division grew in strength and knowledge. Antioxidants were introduced to the industry, and accelerated aging tests entered the scene. Carrying on the labors of the old Rubber Section, test methods were further improved. Physical testing methods occupied much of the energies of the Division during the late 1920's. Throughout the years of its existence, the Division has held numerous symposia on subjects of far-reaching significance to the chemistry of rubber. It has coöperated measurably with the work of rubber men abroad in

efforts to strengthen the world-wide position of the industry. A high spot in this endeavor was the Division's coöperation in the recent Rubber Technology Conference, held in London, England, in May, 1938, under the auspices of the Institution of the Rubber Industry. A large number of meritorious papers were presented by American rubber technologists.

The rapidly growing Division of Rubber Chemistry had become so large by 1927 that it was considered advisable to extend its activities along other channels closely allied with the interest of the rubber chemist. There had been a growing demand for a unit publication in this country to contain all of the technical articles of interest to the rubber chemist and technologist. There had also been a demand for special meetings at geographical points more convenient to the individuals of the industry. Thus, at a divisional meeting in Detroit, Mich., in September, 1927, the executive committee was empowered to proceed with plans for the formation of local groups and for the establishment by the Division of a special publication composed largely of rubber reprints from *Industrial and Engineering Chemistry*. These innovations will be discussed in subsequent sections of this article.

Within the space of these few pages it would be impossible to mention all the names of those active in furthering the work of the Division; nor would it be possible to cover the entire range of its activities and to indicate, except generally, the wide scope covered by the research of its members. The rubber industry owes a large measure of gratitude to the Division of Rubber Chemistry, even to the least of its members, for furthering the science of rubber. The table on page 7 presents a brief résumé of the Division's meetings, with the chairmen and secretaries.

Membership of the Rubber Division on March 31, 1939, totaled 573, consisting of 462 members and 111 associate members.

FORMATION OF LOCAL GROUPS

To carry out the purpose of the Division of Rubber Chemistry to enlarge its activities by means of group organizations, geographically distributed, Harry L. Fisher, division chairman, appointed during the latter part of 1927 local group chairman for the preliminary work in their respective geographical sections as follows: R. P. Dinsmore, Akron; C. R. Boggs, Boston; A. A. Somerville, New York; and R. B. Stringfield, Los Angeles.

New York—January 11, 1928

No time was lost in launching these new enterprises. The first meeting of the New York Group was held January 11, 1928, in New York. With 240 in attendance, organization was effected by the election of W. A. Gibbons as group chairman and D. F. Cranor as secretary-treasurer.

Akron—February 15, 1928

On February 15, the Akron Group held its first meeting in Akron with 300 chemists and engineers attending. H. A. Winkelmann was elected chairman, W. H. Fleming, vice-chairman, and R. J. Bonstein, secretary-treasurer.

Los Angeles—May 11, 1928

Preliminary to organization of the Los Angeles Group, a get-together meeting was held and 43 members were enrolled in the projected group. District organizer,

MEETINGS OF THE DIVISION OF RUBBER CHEMISTRY

Date	Place	Attendance	Chairman	Secretary
Apr., 1919	Buffalo	—	Division authorized by Council, A.C.S.	
Oct., 1919	Philadelphia	—	J. B. Tuttle	A. H. Smith
Apr., 1920	St. Louis	—	W. K. Lewis	A. H. Smith
Sept., 1920	Chicago	100	W. K. Lewis	A. H. Smith
Apr., 1921	Rochester	—	W. W. Evans	A. H. Smith
Sept., 1921	New York	200	W. W. Evans	A. H. Smith
May, 1922	Birmingham	35	C. W. Bedford	A. H. Smith
Sept., 1922	Pittsburgh	140	C. W. Bedford	A. H. Smith
Apr., 1923	New Haven	150	W. B. Wiegand	A. H. Smith
Sept., 1923	Milwaukee	150	W. B. Wiegand	A. H. Smith
Apr., 1924	Washington	150	E. B. Spear	A. H. Smith
Sept., 1924	Ithaca	125	E. B. Spear	A. H. Smith
Apr., 1925	Baltimore	115	C. R. Boggs	A. H. Smith
Feb., 1926	Akron	293	J. M. Bierer	A. H. Smith
Sept., 1926	Philadelphia	300	J. M. Bierer	A. H. Smith
Apr., 1927	Richmond	135	R. P. Dinsmore	A. H. Smith
Sept., 1927	Detroit	192	R. P. Dinsmore	A. H. Smith
Apr., 1928	St. Louis	150	H. L. Fisher	H. E. Simmons
Sept., 1928	Swampscott	300	H. L. Fisher	H. E. Simmons
May, 1929	Columbus	250	A. H. Smith	H. E. Simmons
Sept., 1929	Atlantic City	—	A. H. Smith	H. E. Simmons
Apr., 1930	Atlanta	115	S. Krall	H. E. Simmons
Sept., 1930	Cincinnati	150	S. Krall	H. E. Simmons
Apr., 1931	Indianapolis	150	H. A. Winkelmann	H. E. Simmons
Sept., 1931	Buffalo	175	H. A. Winkelmann	H. E. Simmons
Feb., 1932	Detroit	130	E. R. Bridgwater	H. E. Simmons
Aug., 1932	Denver	55	E. R. Bridgwater	H. E. Simmons
Mar., 1933	Washington	125	L. E. Sebrell	H. E. Simmons
Sept., 1933	Chicago	300	L. E. Sebrell	H. E. Simmons
Mar., 1934	St. Petersburg	85	Ira Williams	H. E. Simmons
Sept., 1934	Cleveland	450	Ira Williams	H. E. Simmons
Apr., 1935	New York	450	S. D. Cadwell	H. E. Simmons
Sept., 1935	Akron	450	S. D. Cadwell	H. E. Simmons
Apr., 1936	Kansas City	75	N. A. Shepard	C. W. Christensen
Sept., 1936	Pittsburgh	350	N. A. Shepard	C. W. Christensen
Apr., 1937	Chapel Hill	125	H. L. Trumbull	C. W. Christensen
Sept., 1937	Rochester	367	H. L. Trumbull	C. W. Christensen
Mar., 1938	Detroit	300	A. R. Kemp	C. W. Christensen
Apr., 1939	Baltimore	350	G. K. Hinshaw	H. I. Cramer
Sept., 1939	Boston	—	G. K. Hinshaw	H. I. Cramer

R. B. Stringfield, was elected temporary president, and E. S. Long, temporary secretary. A meeting of the new group was held on May 11, 1928, and organization was carried out with the adoption of a constitution and by-laws and the official enrollment of 63 members. The first regular officers of the West Coast group were: R. B. Stringfield, president; A. K. Pond, vice-president; E. S. Long, secretary-treasurer; C. R. Park, E. S. Long and A. K. Pond, executive committee.

BOSTON—NOVEMBER 7, 1928

Fourth to carry out organization was the Boston Group, under the direction of C. R. Boggs. The first meeting, held preliminary to official organization, took place on May 9, 1928. There were 285 present, and at the head table sat many well-known rubber men from New England. Formal organization was deterred, owing to the length of the program. At a second meeting on November 7, 1928, the group was officially started, with J. M. Bierer elected chairman and T. M. Knowland, secretary-treasurer.

Chicago—June 28, 1929

The year after the formation of these first four groups, the Chicago Group was organized. A meeting of the general organization committee was held in Chicago on June 28, 1929. The purpose of the group was outlined by the committee as a plan toward closer coöperation between the laboratory and factory through presentation of papers of interest to both factions. The officers elected were: C. Frick, chairman; Otto Urech, vice chairman, and B. W. Lewis, secretary-treasurer. The first meeting of the newly organized group was held on October 25, 1929, at Chicago, in conjunction with a meeting of the Chicago Section of the American Chemical Society.

Detroit—June 23, 1937

With local groups well established in the chief rubber centers of the country, the Division of Rubber Chemistry did not further expand its group organizations until 1937, when the Detroit industrial area, fast growing in prominence as a rubber center, was included in the Division activities through the formation of the Detroit Group. With 75 in attendance, the group held its first meeting on June 23, 1937, and elected the following: chairman, W. J. McCourtney; vice chairman, E. J. Kvet; secretary-treasurer, J. A. Bumpus; chairman of the membership committee, H. C. Anderson; chairman of the entertainment committee, J. H. Norton.

The work of these local groups is well known to all in the rubber industry. They afford an opportunity for supplementing and extending the technical activities of the Division and for those present from the rubber and allied industries to become better acquainted so as to encourage a spirit of coöperation and thus increase the benefits possible from the exchange of ideas.

"RUBBER CHEMISTRY AND TECHNOLOGY"—1928

In the year 1928 which saw the formation of the four local groups, the first issue of *Rubber Chemistry and Technology*, the Division's new journal, was published, Volume 1, No. 1, being dated April, 1928. C. C. Davis, well known to the rubber trade for his contribution in developing the Bierer-Davis oxygen bomb and later for his co-editorship of the A.C.S. Monograph, "The Chemistry and Technology of Rubber", was chosen editor and has remained in that capacity ever since. The service that this valuable publication has rendered during the past eleven years is recognized by the industry, containing as it does reprints of the most important papers on fundamental research, technical developments and chemical engineering problems relating to rubber. In addition to reprints of papers presented in the English language, translations of important foreign language papers are published and occasionally new contributions.

CRUDE RUBBER COMMITTEE—APRIL 23, 1935

The wide variability in crude rubber has always been a source of much trouble to the rubber industry. In the early days the solution of this problem was a hopeless task, with almost numberless varieties of crude rubber on the market, practically all of which contained large amounts of dirt and impurities. As wild rubber became displaced by the plantation grades, there was hope of attaining some degree of uniformity. Two committees of the Division of Rubber Chemistry, The Crude Rubber Testing Committee and the Raw Rubber Specification Com-

mittee, labored on this problem during the 1920's, but achieved little success because of the wide variability of the rubber available and the lack of standard procedures for evaluating quality.

On April 23, 1935, a new Crude Rubber Committee was appointed by S. M. Cadwell, Chairman of the Division of Rubber Chemistry, who acted on the suggestion of Edgar Rhodes, of the Rubber Research Institute of Malaya, that American rubber consumers organize for closer coöperation with those engaged in crude rubber production. The new committee, headed by Harold Gray, was delegated to promote a better understanding between producers and consumers of crude rubber, to facilitate the exchange of information on the quality requirements for various crude rubbers, including latex, and to discuss quality requisites with technical agencies allied with producers, methods of testing and evaluation of new types of rubber and latex. Since its origin, this committee has accomplished much through coöperation with producers in increasing the uniformity of crude rubber and in outlining procedures to determine the quality of crude rubber and latex. There is more to be done along this line, and the present activities of the Committee, now headed by R. H. Gerke, indicate that every effort is being made to further this work.

THE A. C. S. MONOGRAPH ON THE CHEMISTRY AND TECHNOLOGY OF RUBBER—1937

In 1937 the appearance of the American Chemical Society Monograph on "The Chemistry and Technology of Rubber" marked the completion of one of the most important single tasks sponsored by the Division of Rubber Chemistry.

The publication of a monograph on rubber by the Division was first suggested by H. E. Howe, Editor of *Industrial and Engineering Chemistry*, at a meeting of the Division of Rubber Chemistry in 1928. After considerable planning and preliminary work, C. C. Davis was appointed editor-in-chief of the Monograph in 1934, and he in turn appointed J. T. Blake as associate editor. Twenty-six authors, selected from authorities in various countries, were invited to contribute chapters on various subjects. That this book is now considered to be the most authoritative, informative and complete treatise on the chemistry and technology of rubber is unquestioned. To the editors and authors who gave unselfishly, and without remuneration of their time and energy, much well-deserved credit is due.

GOODYEAR CENTENNIAL MEETING—SEPTEMBER, 1939

The Division of Rubber Chemistry, with its parent organization, celebrated at the regular Fall meeting of the Society, September 11 to 15, 1939, at Boston, Massachusetts, the centenary of the discovery of vulcanization by Charles Goodyear, and thus paid tribute to one of America's great sons, whose pioneer work made our present-day rubber industry possible.

At the Goodyear Centennial meeting new by-laws were adopted. Although not materially changing the practices carried on in the past, the by-laws provide for certain new committees (membership, nomenclature and planning) and make it possible for the Division to operate officially under the recently-obtained national charter of the American Chemical Society.

Since the formation of the old Rubber Chemistry Section of the American Chemical Society thirty years ago, we have seen the rubber industry in all its

phases undergo a tremendous growth, both industrially and scientifically. It would not be unfair to say that this far-reaching development has been materially assisted by the activities of an organized group of rubber chemists within the American Chemical Society. As long as the spirit of coöperation and contribution toward technical development is maintained within this body, we need have no fear for the future of the rubber industry.

MOLECULAR WEIGHT OF SOL AND GEL IN CRUDE HEVEA RUBBER *

A. R. KEMP and H. PETERS

BELL TELEPHONE LABORATORIES, NEW YORK, N. Y.

In a previous article[1] a simple procedure for determining the sol rubber content of *Hevea* latex and crude rubber was described. This method is based on the fact that the sol rubber diffuses into a solvent, such as petroleum ether or hexane, in which the rubber is placed. The solution can be readily decanted from the highly swollen gel, so by periodic change to fresh solvent it is possible to fractionate the sol content into numerous fractions, depending on their relative solubility and rate of diffusion into the solvent.

In the present investigation the molecular weights of sol rubber fractions in hexane were determined by the well-known viscosity method developed by Staudinger[2]. This method has been proved satisfactory in the case of numerous polymeric substances in the range of molecular weights capable of being checked by standard methods. Several investigators, however, have questioned on theoretical grounds its absolute accuracy for extremely high polymers such as natural rubber. It can be said in support of Staudinger's work that the average molecular weight of crude rubber, determined by the osmotic pressure and ultracentrifuge methods, is of the same order as shown by the viscosity method. In spite of the lack of proof that the viscosity method gives the true molecular weight of extremely high polymeric substances, it is of utmost value in providing a simple procedure for comparative purposes. The work on the viscosity molecular weight of crude rubber has so far been confined to the determination of the viscosity of very dilute dispersions of whole crepe or smoked sheet in benzene, toluene or tetralin. These dispersions have been prepared by first allowing the rubber to imbibe the solvents and swell, followed by shaking the liquid vigorously to break up the swollen gel and disperse it, while at the same time the sol portion has entered into solution. The refractive indices of these solvents are so close to that of rubber hydrocarbon that it is very difficult to determine when the dispersion is complete. Staudinger apparently has favored tetralin over other solvents, since it appears to disperse the gel more completely. It is very difficult to disperse completely the gel of high-quality plantation crude rubber in benzene or toluene in the absence of oxygen, and for this reason the use of these solvents is not advisable. The influence of the dispersed gel on the viscosity is likely to be a variable, depending on the size of the gel aggregates and the amount present. On the other hand, some types of plantation crepes of high sol content will disperse readily in benzene.

It will be shown that the viscosity of dilute crude rubber dispersions in tetralin decreases rapidly in spite of the fact that care is taken to exclude oxygen. Tetralin is objectionable on account of its relatively high viscosity. It is likely to contain difficultly removable, chemically active substances which catalyze the oxidation breakdown of the rubber hydrocarbon, thereby reducing its molecular weight.

In the present work the gel rubber was completely excluded by employing the diffusion process of separating the sol from the gel and of separating the sol

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into fractions of increasing molecular weight and decreasing solubility. Hexane was employed as the solvent on account of its complete inertness, non-polarity, ease of handling and its ability to fractionate clearly the sol from the gel, leaving all solid non-hydrocarbon substances in the gel skeleton. The hexane solutions were perfectly clear, except for a faint opalescence due to the Tyndall effect of colloidal solutions.

PROCEDURE

An Ostwald viscometer placed in a water bath held at 25° C.±0.1° was employed. Exactly 5 cc. of solution was pipetted into the viscometer for each determination. Great care was taken in cleaning the viscometer between runs and to avoid the entrance of fibers or dirt particles into the viscometer. The length of the capillary of the viscometer was 103.0 mm.; its bore was 0.066 to 0.067 mm. The times of flow in seconds at 25° C. for different liquids were as follows: distilled water, 95.2; *n*-hexane, 50.7; benzene, 72.7; tetralin, 215.4. The *n*-hexane is known as Skellysolve. It was obtained from the Skelly Oil Company and had a boiling range of 66° to 70° C.

A uniform sheet of R.C.M.A.* crepe was selected for the fractionating experiments, and adjacent sheets from the same bale were employed in the milling experiments. The apparatus and procedure employed in the extraction of the sol fractions by *n*-hexane was the same as that previously described by the authors[1]. The concentration of sol in the hexane solutions was accurately determined by evaporating definite volumes to dryness to a constant weight of residue. Wherever necessary the acetone extract was made on the residue to determine the amount of "resin substances present". The concentrations of the solutions were adjusted to those required for the viscosity measurements by exactly controlled dilution with hexane.

Since the rate of diffusion of sol into hexane is most rapid for fractions having the lowest molecular weight, the time of extraction for each fraction was increased as fractionation proceeded. Care was taken to exclude light from the solutions and air was displaced over the solutions with a stream of nitrogen. Viscosities were measured as soon as possible after decanting the solution from the swollen gel.

The average molecular weight was calculated by the use of the Staudinger formula.

$$M = \frac{\eta_{sp}}{C \cdot 3 \times 10^{-4}}$$

where C is the base molal concentration, *i.e.*, one mole is taken as 68 grams of rubber hydrocarbon base unit (C_5H_8) per liter. The value 3×10^{-4} is Staudinger's K_m constant, which varies with the material, and in this case is the value found when equating the viscosity molecular weight of low-molecular broken-down rubber with the molecular weight as determined by the freezing point method. The average molecular weight was also calculated by the formula based on the Arrhenius equation:

$$\frac{\log \eta_r}{C} = Kc$$

In this case:

$$M' = \frac{\log_{10} \eta_r \cdot 10^4}{C}$$

* R.C.M.A.=Rubber Culture Maatschappij Amsterdam.

Excellent agreement in duplicate viscosity runs was obtained using hexane solutions. In the more dilute solutions, where η_r was less than about 3, variations were not over ± 0.1 sec. With the more viscous solutions, which had a value for η_r of 3 or more, the duplicate values were not so close but they were very satisfactory.

MOLECULAR WEIGHT RANGE OF SOL IN CREPE

The results shown in Tables I and II show that the particular lot of R.C.M.A. crepe studied contains sol rubber, which can be separated into fractions having an average molecular weight range of 78,000 to 213,000. The presence of acetone-soluble substances apparently had little effect on the results. When M and M' were plotted against relative viscosity, it was found that the curves crossed in every case at η_r varying between 1.66 and 1.70. The molecular weight values selected, given in parentheses, were those corresponding to these relative viscosities. When the relative viscosity of the solution is 1.6615, M becomes equal to

TABLE I

VISCOSITY MOLECULAR WEIGHT OF HEXANE-SOLUBLE FRACTIONS FROM WHOLE UNMILLED R.C.M.A. CREPE

Base molarity C	Rate of flow (seconds)	η_r	$M=\frac{\eta_{sp}}{C\cdot 3\times 10^{-4}}$	Molecular weight values selected	$M'=\frac{\log_e \eta_r \cdot 10^4}{C}$
2.5-HR. EXTRACT (12.7 PER CENT)					
0.0158	68.2	1.345	72,700	(80,000)	81,500
0.0211	75.2	1.483	76,300		81,100
0.0316	90.4	1.783	82,500		79,500
0.0632	152.7	3.011	106,000		75,500
1-DAY EXTRACT (30.3 PER CENT)					
0.00908	67.7	1.335	123,000	(138,000)	138,000
0.0109	71.9	1.418	128,000		139,000
0.0136	78.3	1.544	133,000		139,000
0.0182	89.7	1.769	141,000		136,000
0.0273	116.8	2.303	159,000		133,000
0.0545	240.2	4.737	229,000		124,000
8-DAY EXTRACT (44.2 PER CENT)					
0.00515	63.1	1.244	158,000	(187,000)	184,000
0.00687	68.0	1.341	165,000		185,000
0.0103	79.2	1.562	182,000		188,000
0.0206	120.6	2.378	223,000		183,000
0.0412	262.2	5.171	337,000		173,000
13-DAY EXTRACT (49.0 PER CENT)					
0.00228	56.8	1.120	175,000	(210,000)	216,000
0.00343	59.6	1.176	171,000		205,000
0.00457	63.7	1.256	187,000		217,000
0.00685	70.5	1.391	190,000		209,000
0.0137	98.3	1.939	229,000		210,000
21-DAY EXTRACT (53.0 PER CENT)					
0.00900	76.3	1.505	187,000	(197,000)	197,000
0.0101	80.0	1.578	191,000		196,000
0.0135	93.6	1.846	209,000		197,000

TABLE II

VISCOSITY MOLECULAR WEIGHT OF HEXANE-SOLUBLE FRACTIONS OF UNMILLED ACETONE-EXTRACTED R.C.M.A. CREPE

Base molarity C	Rate of flow (seconds)	η_r	$M=\frac{\eta_{sp}}{C \cdot 3\times10^{-4}}$	Molecular weight values selected	$M'=\frac{\log_{10}\eta_r \cdot 10^4}{C}$
1-HR. EXTRACT (4.4 PER CENT)					
0.0140	65.6	1,293	69,700		82,900
0.0210	74.8	1.475	75,400		80,400
0.0280	84.4	1.664	79,000	(78,000)	79,000
0.0420	107.5	2.120	89,000		77,700
0.0840	205.4	4.051	121,000		72,300
2-HR. EXTRACT (12.9 PER CENT)					
0.0100	66.7	1.303	101,000		115,000
0.0150	76.3	1.504	112,000	(115,000)	118,000
0.0300	110.9	2.187	132,000		113,000
0.0600	211.0	4.161	176,000		103,000
4-HR. EXTRACT (18.6 PER CENT)					
0.0105	67.7	1.335	106,000		120,000
0.0157	75.5	1.489	104,000	(115,000)	110,000
0.0315	115.5	2.278	135,000		114,000
0.0630	232.4	4.583	190,000		105,000
7-HR. EXTRACT (23.4 PER CENT)					
0.00866	66.6	1.313	121,000		137,000
0.0130	76.2	1.503	129,000	(134,000)	136,000
0.0260	110.8	2.190	153,000		131,000
0.0520	220.2	4.343	214,000		123,000
2-DAY EXTRACT (30.0 PER CENT)					
0.00525	62.7	1.236	156,000		175,000
0.0105	76.9	1.517	164,000		172,000
0.0140	88.2	1.740	176,000	(172,000)	172,000
0.0210	114.8	2.264	201,000		169,000
0.0840	849.0	16.746	625,000		146,000
4-DAY EXTRACT (37.0 PER CENT)					
0.00570	64.4	1.270	158,000		182,000
0.00718	68.4	1.349	162,000		181,000
0.00957	75.4	1.487	170,000	(179,000)	180,000
0.0144	91.4	1.803	186,000		178,000
0.0287	160.1	3.156	250,000		174,000
0.0574	—	—	—		—
9-DAY EXTRACT (42.4 PER CENT)					
0.00335	59.1	1.166	158,000		199,000
0.00503	63.8	1.258	171,000		198,000
0.00719	70.6	1.393	182,000	(197,000)	200,000
0.0126	89.7	1.769	203,000		197,000
0.0168	107.5	2.120	222,000		194,000
—	—	—	—		—

TABLE II—*Continued*

Base molarity C	Rate of flow (seconds)	η_r	$M=\frac{\eta_{sp}}{C\cdot 3\times 10^{-4}}$	Molecular weight values selected	$M'=\frac{\log_{10}\eta_r\cdot 10^4}{C}$
		14-DAY EXTRACT (46.4 PER CENT)			
0.00554	65.7	1.296	178,000	(206,000)	203,000
0.00776	73.3	1.446	192,000		206,000
0.0129	93.3	1.840	217,000		205,000
0.0194	125.4	2.474	253,000		203,000
		16-DAY EXTRACT (47.8 PER CENT)			
0.00953	80.4	1.586	205,000	(210,000)	211,000
0.0143	100.8	1.988	230,000		209,000
		20-DAY EXTRACT (49.0 PER CENT)			
0.00870	75.9	1.497	190,000	(201,000)	201,000
0.0116	86.7	1.710	204,000		201,000
		30-DAY EXTRACT (50.3 PER CENT)			
0.00942	79.3	1.564	200,000	(207,000)	206,000
0.01259	92.2	1.820	219,000		208,000
		48-DAY EXTRACT (52.4 PER CENT)			
0.0115	88.8	1.751	218,000	(213,000)	212,000
0.0172	118.0	2.327	257,000		213,000

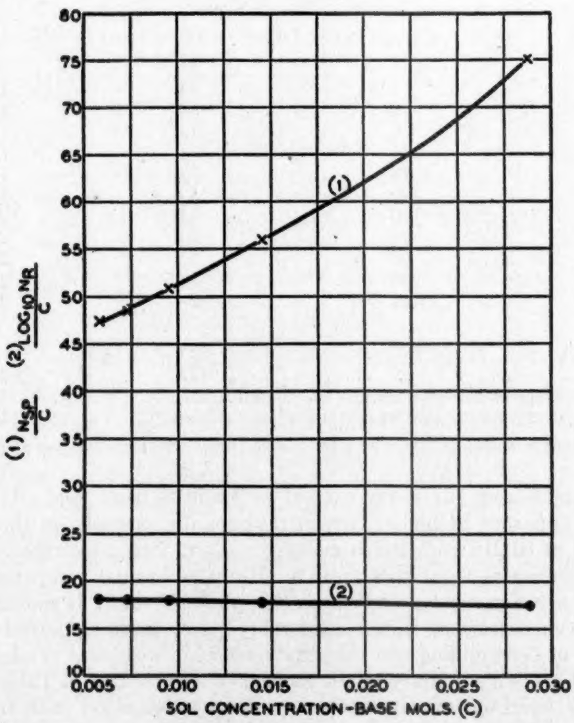

FIG. 1.—Relation between viscosity and concentration of solutions of sol rubber in hexane.

M', as is seen by inserting the log of this value and the value of 0.6615 for the specific viscosity in the two equations. It will be noted that the average molecular weight calculated by the Staudinger equation showed a greater deviation with change in concentration than in the case of the values based on the Arrhenius equation. In other words, the deviation of η_{sp}/C from constancy at various concentrations was much greater than $\log_{10} \eta_r/C$, as is shown in Figure 1, in

Table III

Summary of Molecular Weight Data on Hexane-Soluble Fractions of Crepe Rubber

Fraction no.	Extraction period (hours)	Extract (per cent)	Molecular weight calculated at η_r of 1.7
	R.C.M.A. crepe		
1	2.5	12.7	80,000
2	21.5	17.6	138,000
3	168.0	13.9	187,000
4	120.0	4.8	210,000
5	192.0	4.0	197,000
Total extract		53.00	
Residue		47.0	>210,000
Weighted average molecular weight of extract			148,000
Weighted average molecular weight of whole rubber *			177,000
	R.M.C.A. crepe (acetone-extracted)		
1	1	4.4	78,000
2	1	8.5	115,000
3	2	5.7	115,000
4	3	4.8	134,000
5	41	6.6	172,000
6	48	7.0	179,000
7	120	5.4	197,000
8	120	4.0	206,000
9	48	1.4	210,000
10	96	1.2	201,000
11	240	1.3	207,000
12	432	2.1	212,000
Total extract		52.4	
Residue		47.6	>212,000
Weighted average molecular weight of extract			156,000
Weighted average molecular weight of whole rubber *			192,000

* Using molecular weight of last extract for that of residual gel; proteins and resins ignored.

which the data from the 4-day extract in Table II were used. This deviation is even more apparent at higher concentrations; for example, in the 2-day extract in Table II at 0.0210 and 0.0840 molarity. η_{sp}/C increases from 29 to 271, while $\log_{10} \eta_r/C$ decreases from 16.9 to 14.6. Many additional comparisons leading to the same conclusion can be made from the tabulated data. It should be noted that the lowest concentrations were considerably below those employed by Staudinger and others in determining the viscosity molecular weight of crude rubber.

Table III gives a summary of the molecular weight data in Tables I and II and includes the weighted average molecular weights based on each fraction. It has been assumed in this case that the gel has a molecular weight equal to that of

the extract giving the highest molecular weight. The authors believe, however, that the molecular weight of the gel is higher than this value.

The molecular weight distribution will depend on the particular rubber under test and on the fractionation procedure. For example, when 5 grams of finely cut, acetone-extracted, yellow crepe of high sol content was placed in 250 cc. of hexane, 3.0 per cent sol was extracted in 1 hour at room temperature. This sol was found to have a molecular weight of 63,000. When Brazilian fine para of low sol content was similarly treated for 2 hours, 1.7 per cent sol of a molecular weight of 64,000 diffused into the hexane.

TABLE IV

VISCOSITY MOLECULAR WEIGHT OF MASTICATED CREPE * IN DIFFERENT SOLVENTS

Base molarity C	Rate of flow (seconds)	η_r	$M=\frac{\eta_{sp}}{C\cdot 3\times10^{-4}}$	Molecular weight values selected	$M'=\frac{\log_{10}\eta_r\cdot 10^4}{C}$
HEXANE, 50.7 SEC.					
0.0500	71.5	1.410	27,300	(30,000)	29,800
0.0625	77.8	1.535	28,500		29,800
0.0833	90.2	1.779	31,200		30,000
0.2500	240.0	4.779	49,700		27,000
BENZENE, 72.7 SEC.					
0.0500	107.4	1.477	31,800	(33,000)	33,900
0.0625	117.9	1.621	33,000		33,600
0.0833	137.0	1.884	35,400		33,000
0.2500	369.0	5.075	54,300		28,200
TETRALIN, 215.4 SEC.					
0.0500	320.2	1.486	32,400	(33,000)	34,400
0.0625	348.0	1.615	32,800		33,300
0.0833	401.4	1.864	34,600		31,300
0.2500	1059.0	4.916	52,200		27,600

* 300-g. batch of R.C.M.A. crepe broken down for 25 minutes on cool laboratory mill rolls with separation of 0.035 inch.

VISCOSITY OF MILLED CREPE IN HEXANE, BENZENE AND TETRALIN

Since the Staudinger K_m constant of 3×10^{-4} was established on broken-down rubber in benzene and tetralin, a comparison of the viscosities of a sample of milled crepe was made in these solvents with the viscosity of the same rubber in *n*-hexane. These results are shown in Table IV. It was felt that the agreement of the results in hexane with those in the other solvents was sufficiently close to justify employing the Staudinger K_m constant in calculating the molecular weight from the viscosity data of the hexane solutions. The average molecular weight calculated from the hexane solutions was about 10 per cent lower than that given by the benzene and tetralin solutions. Further work would be required to determine the cause of this difference.

Benzene and tetralin are satisfactory solvents for viscosity molecular weight studies of well-masticated rubber, since this rubber is completely soluble in these solvents and resists further oxidative breakdown in tetralin on account of having been already oxidized during mastication.

MOLECULAR WEIGHT OF MILLED CREPE FRACTIONS

Fractionation of milled crepe was carried out by the procedure already referred to[1]. The molecular weight data on these fractions are given in Table V. These data show that a thorough breakdown on the mill results in a product which has a rather narrow range of molecular weight. This might be expected, since the highest polymers offer the greatest frictional resistance and would be the most rapidly broken down. The low polymers, on the other hand, would constitute the plastic phase. Data of this kind are very valuable in the study of rubber breakdown under various conditions. If the same rubber is broken down under the

TABLE V

VISCOSITY MOLECULAR WEIGHT OF HEXANE-SOLUBLE FRACTIONS OF MILLED CREPE *

Base molarity C	Rate of flow † (seconds)	η_r	$M=\frac{\eta_{sp}}{C\cdot 3\times 10^{-4}}$	Molecular weight values selected	$M'=\frac{\log_{10}\eta_r\cdot 10^4}{C}$
		0.5-HR. EXTRACT (1.6 PER CENT)			
0.00588	52.3	1.032	18,100		23,300
		2.5-HR. EXTRACT (7.6 PER CENT)			
0.00690	53.2	1.049	23,700		30,110
0.0103	54.3	1.071	23,000		28,900
0.0207	58.2	1.147	23,700		28,700
		7-HR. EXTRACT (36.5 PER CENT)			
0.0212	60.8	1.200	31,400		37,300
0.0425	73.7	1.453	35,500	(37,000)	38,200
0.0850	105.5	2.080	42,300		36,200
		1-DAY EXTRACT (83.7 PER CENT)			
0.0233	62.3	1.228	32,600		38,300
0.0350	70.0	1.380	36,200	(39,000)	40,000
0.0700	95.0	1.874	41,600		39,000
0.1400	167.0	3.294	54,600		37,000
		R.C.M.A. BROKEN-DOWN (WHOLE RUBBER)			
0.0375	70.0	1.380	37,000		37,300
0.0502	77.9	1.536	35,600	(39,000)	37,100
0.0750	95.3	1.880	39,200		36,500
0.301	449.4	8.864	87,000		31,400

* 300-g. batch of R.C.M.A. crepe broken down for 15 minutes on cool laboratory mill rolls with separation of 0.085 inch.
† Hexane, 50.7 seconds.

same milling conditions at higher temperatures, the range of molecular weights is greater and the average of the whole milled rubber is higher. These data are given in Table VI and explain why it is possible as a rule to obtain, with hot milled rubber, vulcanizates superior to those obtained with cold milling when other conditions are equal. The reduced breakdown at 96° C. as compared with 35° C. is believed to be due mainly to lower frictional forces. A different type of breakdown occurs at 142° C. Considerable fumes are given off and the rubber becomes reddish brown in color. Figure 2 shows the relative rates of hexane extraction of the hot and cool milled rubber under conditions already described[1].

STABILITY OF RUBBER IN HEXANE AND TETRALIN

Hexane solutions of sol rubber showed relatively little change in viscosity on standing, compared with crude rubber dispersed in tetralin. Changes in hexane

TABLE VI

EFFECT OF MILLING TEMPERATURE ON MOLECULAR WEIGHT OF HEXANE FRACTIONS OF MASTICATED CREPE *

Extraction period (hours)	Extract (per cent)	Base molarity	η_r	M'
I. AVERAGE MILL ROLL TEMPERATURE = 35° C.				
3	17.6	0.0725	1.751	33,500
7	55.0	0.0684	1.848	39,000
24	23.0	0.0690	1.830	38,000
II. AVERAGE MILL ROLL TEMPERATURE = 96° C.				
3	8.4	0.0475	1.848	56,100
7	9.1	0.0325	1.696	70,600
24	30.2	0.0311	1.692	73,400
48	13.3	0.0391	1.968	75,200
144	29.6	0.0356	1.915	79,000
168	7.5	0.0212	1.460	77,500
III. AVERAGE MILL ROLL TEMPERATURE = 142° C.				
3	31.4	0.0480	1.927	59,400
7	25.9	0.0390	1.799	65,400
24	18.5	0.0376	1.744	64,300
48	6.5	0.0200	1.375	69,200
144	3.2	0.0116	1.212	63,000
Residue (gel)	14.5			

* 300 g. of R.C.M.A. crepe broken down for 15 minutes on laboratory mill with roll opening of 0.089 cm.:

	I	II	III
Initial roll temperature, ° C.	32	99	138
Final roll temperature, ° C.	38	98	146
Final rubber temperature, ° C.	43	90	140
Williams plasticity after standing 3 days, mm.	1.90	4.37	3.81

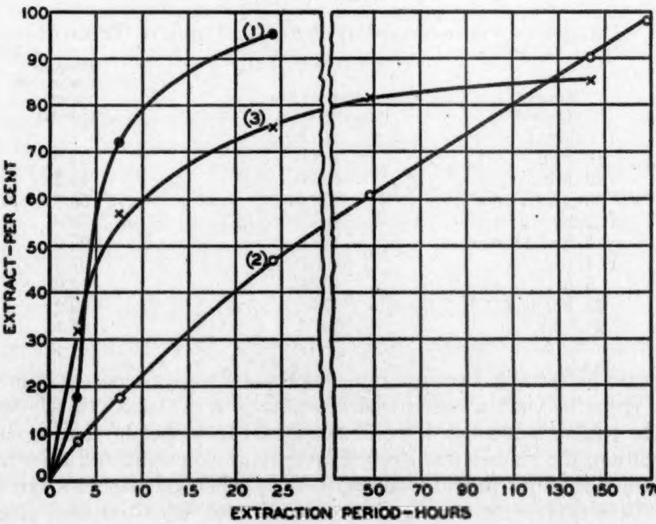

FIG. 2.—Extraction of sol rubber in milled crepe: (1) milled at 35° C.; (2) milled at 96° C.; (3) milled at 142° C.

solutions are shown in Table VII. In these experiments the air above the solutions was not displaced with nitrogen, since this would remove hexane and change the concentration. The solutions were exposed to diffused light in tightly stoppered flasks. It is to be noted that the maximum change in the relative viscosity of any of these solutions after long standing is less than 2 per cent. Since the air was displaced from over the hexane during the extraction periods and the solution was protected from light, it is believed that changes in viscosity during extraction were not significant.

TABLE VII

CHANGE IN VISCOSITY OF HEXANE SOLUTIONS OF RUBBER ON STANDING

Concentration base molarity C	Time of flow (seconds)	Time of standing (hours)	Difference in flow time (seconds)
0.0632	152.7 *		
0.0632	152.5	20	0.2
0.0632	150.6	96	2.1
0.0545	240.2 *		
0.0545	235.7	72	4.5
0.0136	78.3 *		
0.0136	77.9	72	0.4
0.0136	77.1	456	1.1
0.0140	88.2 *		
0.0140	86.7	360	1.5
0.0105	76.9 *		
0.0105	76.0	96	0.9
0.00228	56.8 *		
	56.5	120	0.3
0.0115	88.8 *		
0.0115	88.8	24	0.0

* Original value.

TABLE VIII

CHANGE IN VISCOSITY OF 0.17 PER CENT CREPE IN TETRALIN

Time of standing	Rate of flow (seconds)	Difference from original value (seconds)
Original	513.8	
10 min.	491.0	22.8
20 min.	465.6	48.2
30 min.	450.0	63.8
2 hr.	428.8	85.0
2 hr., 11 min.	418.8	95.0
4 hr.	406.0	107.8
5 hr.	401.8	112.0
23 hr.	374.4	139.4
24.5 hr.	367.7	146.1

In the case of tetralin two separate dispersions were prepared from unmilled R.C.M.A. crepe to yield a base molal concentration of 0.025. In the case of one solution the rubber was swelled for 72 hours and then shaken. In the case of the second solution, the rubber was swelled in tetralin overnight and then frequently shaken during a 2-hour period to disperse the swollen gel particles. In each case the first viscosity reading was made a few minutes after the final shaking and the change was then noted on repeated measurements at short intervals for longer periods. The results of changes in viscosity of the first solution are shown in Table VIII. These results indicate that tetralin is entirely unsuited to determina-

tions of the molecular weight of crude rubber. The molecular weights calculated from the first viscosity measurements made on these solutions are as follows: $M = 185,000$ and $182,000$; $M' = 151,000$ and $150,000$. However, the rapid decrease in viscosity of the first solution gives values for M of 94,000 and M' of 93,000 after standing 24.5 hours. The rubber macro-molecule is very sensitive to oxidation. The nitrogen used in this case to remove the air above the solution was the same as used in the case of hexane solutions. It appears that the use of tetralin may require a complete removal of oxygen to prevent breakdown of the rubber; this is a condition difficult to realize. The large decrease of viscosity following repeated measurements was surprising and unexpected. This change may be due to a shearing effect on the dispersed gel in addition to an oxidation effect. The authors were unable to find this effect previously mentioned in the case of tetralin dispersions of crude rubber, although Staudinger[2] followed the viscosity changes of rubber in tetralin over long periods of time. Broken-down rubber in tetralin

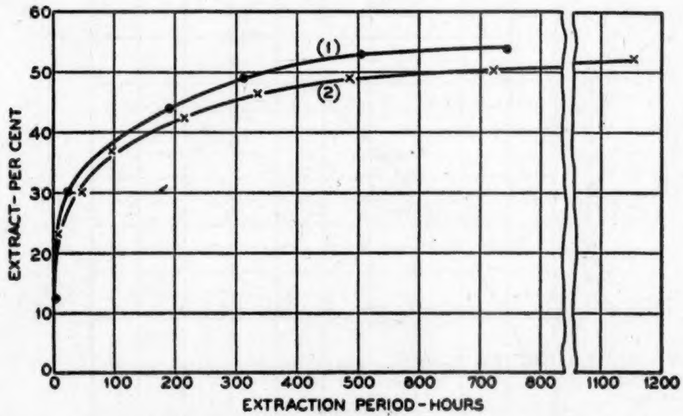

FIG. 3.—Extraction of sol rubber from crepe with hexane: (1) whole R.C.M.A. crepe; (2) acetone-extracted R.C.M.A. crepe.

did not show these changes. Since broken-down rubber is already oxidized and is free from gel, it would be expected to resist further oxidation. It is concluded that the effects noted in the case of crude rubber in tetralin are due to the influence of the dispersed gel and to a rapid breakdown of the large rubber molecules. Staudinger and Bondy[3] have already noted great reductions in the viscosity of high-molecular rubber in tetralin on standing.

MOLECULAR WEIGHT OF GEL RUBBER

The hexane extraction of crepe was carried out for somewhat longer periods than are shown in Tables I and II. The rate of extraction steadily diminishes, as is shown in Figure 3. Whether the added extract is due to sol rubber present originally or to an oxidative breakdown of the gel is not known. The authors[1] have already shown the ease of converting gel to sol by oxidation. Small amounts of oxygen present in the nitrogen might be sufficient to cause gel-sol conversion. On the other hand, the steadily diminishing amount of extract indicates a very slow extraction of the larger sol molecules. These results show that when the molecular weight exceeds 200,000 the solubility of rubber is very low. It appears

that the molecular weight of gel rubber is greater than 210,000. It is impossible to do much more than speculate on the molecular weight range of gel rubber. However, if the molecular weight values of sol rubber fractions given in Tables I and II are plotted as was done in Figures 4 and 5, extrapolation of the curves indicates that the molecular weight of gel rubber may reach 300,000 or more.

The authors have already shown[1] that the rubber hydrocarbon in carefully prepared latex films is gel. Only about 3 per cent of sol rubber is present. This

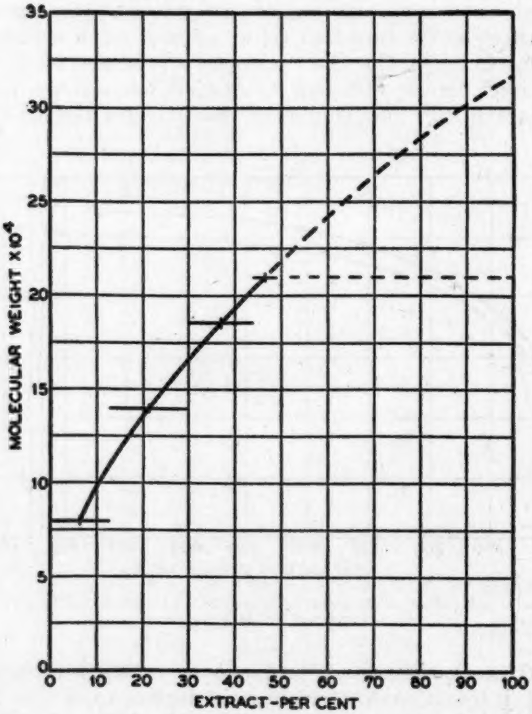

FIG. 4.—Variation of molecular weight of successive fractions of sol rubber from crepe.

gel has not been passed through rolls, as is the case with the gel remaining in crude plantation rubber, so that one would expect it to be of a higher molecular order than the residual gel in crude rubber. Gel, of course, can exist in a range of molecular weights as well as sol. Some evidence that indicates that latex contains gels of varying molecular complexity is given in Figure 7. In this case it is shown that gel can be fractionated in hexane which contains 10 per cent of absolute alcohol and that the solubility diminishes as extraction proceeds. This evidence, together with that recently obtained[1] showing the high resistance of a portion of latex gel to oxidation, leads to the conclusion that the rubber gel in latex is present in variable molecular sizes.

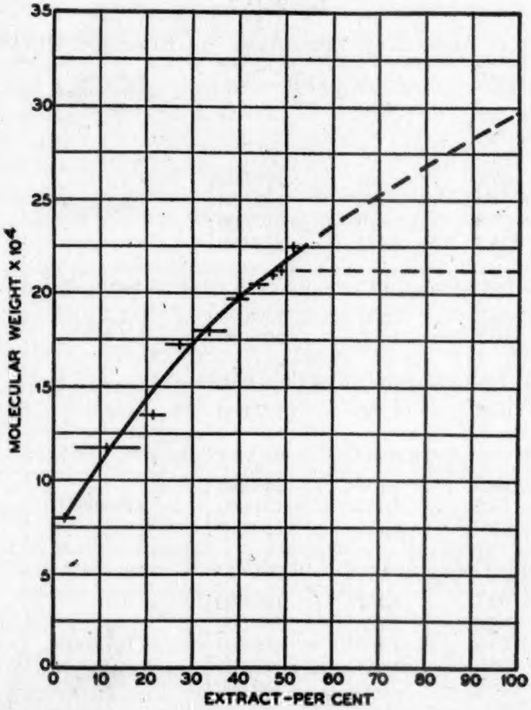

FIG. 5.—Variation of molecular weight with successive fractions of sol rubber from acetone-extracted crepe.

EFFECT OF ABSOLUTE ETHYL ALCOHOL ON THE VISCOSITY OF HEXANE SOLUTIONS

The reduction in the viscosity of rubber cements by addition of polar solvents such as alcohols and ketones is well known. The effect of adding various quantities of absolute alcohol to the 14-day hexane fractions from the acetone-extracted R.C.M.A. shown in Table II was studied. These results are given in Table IX. The effect on the calculated molecular weight is shown in Figure 6. In these experiments the viscosities were first measured in the absence of alcohol, then alcohol was added and the viscosities were measured immediately. It can therefore be stated that the decrease in relative viscosity due to the alcohol is immediate. These data show the importance of avoiding the presence of a polar solvent in viscosity molecular weight determinations.

EFFECT OF POLAR SOLVENTS ON GEL-SOL CONVERSION

The effect of adding 10 per cent of absolute ethyl alcohol on the extraction of dried latex film rubber was studied. The extraction was carried out by the procedure recently described by the authors[1]. The results in Figure 7 show the very great influence of alcohol on the peptizing of gel rubber. Experiments showed that when the hexane and alcohol were carefully removed by evaporation in nitrogen to avoid oxidation, the residual rubber was practically insoluble in hexane and behaved like gel.

TABLE IX

EFFECT OF ALCOHOL ON VISCOSITY OF SOL RUBBER IN HEXANE

Base molarity C	Rate of flow (seconds)	η_r	$M=\frac{\eta_{sp}}{C\cdot 3\times 10^{-4}}$	Molecular weight values selected	$M'=\frac{\log_{10}\eta_r\cdot 10^4}{C}$
HEXANE, 50.7 SEC.					
0.00554	65.7	1.296	178,000	(206,000)	203,000
0.00776	73.3	1.446	192,000		206,000
0.0129	93.3	1.840	217,000		205,000
0.0194	125.4	2.474	253,000		203,000
99.75 PER CENT HEXANE + 0.25 PER CENT ALCOHOL, 50.7 SEC.					
0.0129	85.3	1.682	176,000	(175,000)	175,000
0.0194	110.2	2.173	202,000		174,000
98 PER CENT HEXANE + 2 PER CENT ALCOHOL, 51.2 SEC.					
0.00698	64.8	1.266	127,000	—	147,000
95 PER CENT HEXANE + 5 PER CENT ALCOHOL, 51.6 SEC.					
0.00698	64.9	1.258	123,000	(139,000)	143,000
0.0116	75.1	1.455	131,000		140,000
0.0175	89.6	1.736	140,000		137,000
90 PER CENT HEXANE + 10 PER CENT ALCOHOL, 54.2 SEC.					
0.00499	62.7	1.157	105,000	(127,000)	127,000
0.00698	66.3	1.223	107,000		125,000
0.0116	75.8	1.400	115,000		126,000
0.0175	90.4	1.668	127,000		127,000
0.0349	138.8	2.560	149,000		117,000

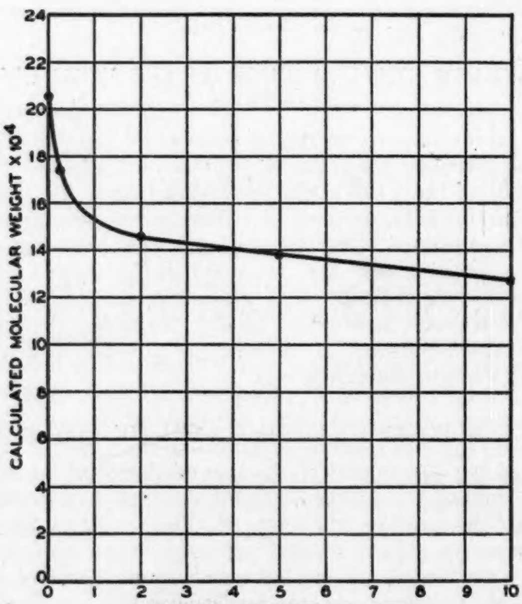

FIG. 6.—Effect of adding alcohol to hexane solutions of sol rubber on the viscosity molecular weight.

Latex film rubber weighing 3.5 grams, which had been completely extracted with hexane, was then extracted with 250 cc. of hexane containing 50 cc. of acetone for 3 days. At the end of this time the solution was decanted from the gel and the rubber was precipitated from it by addition of acetone. This rubber was dried to constant weight in a stream of nitrogen at room temperature. It amounted to 29.6 per cent of the original sample. The extraction was repeated with fresh solvent for 5 days, but no further rubber was extracted. It is apparent from this experiment that acetone is not as effective in peptizing gel as is ethyl alcohol; this might be expected, since alcohol is more polar than acetone.

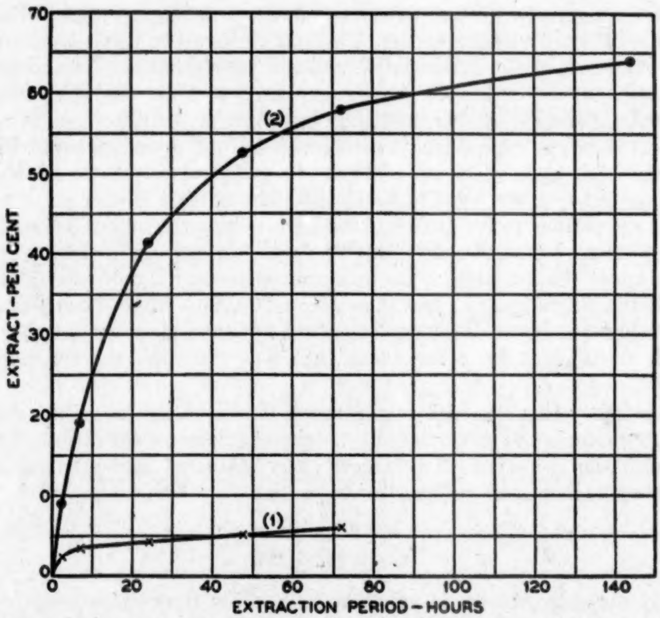

FIG. 7.—Effect of alcohol on the solubility of gel rubber in hexane; (1) gel rubber in hexane; (2) gel rubber in hexane plus 10 per cent of absolute ethyl alcohol.

The most logical explanation for the peptizing effect of polar solvents on rubber gel is that there is a large reduction in van der Waals forces resulting from the presence of polar groups. A change in the shape of the rubber molecules might also occur. There is, however, no concrete evidence available to indicate such a change.

SWELLING IN SOLVENTS

The literature contains many references to the swelling of crude rubber in various organic solvents. Values ranging from a few hundred to a few thousand per cent swelling are to be found. Our experience has been that the swelling in a given solvent is a property of the gel and depends on the amount and nature of this gel present.

When the residual gel from the complete extraction of crepe by hexane was treated with a mixture of hexane containing 15 per cent of acetone, 22 per cent of this gel dissolved in 2 hours. The rubber was precipitated from solution with acetone, and the acetone was completely removed in a stream of nitrogen at room

temperature. A 1.8-gram sample of this rubber was covered with 300 cc. of hexane. No rubber diffused into the hexane, but the rubber absorbed all of the solvent, and it had the properties of a thick stringy gel on shaking. Before solution the gel rubber had swelled about 2000 per cent in hexane; however, after the peptizing treatment and removal of the peptizing agent (*i.e.*, acetone), the swelling reached a point of over 16,000 per cent. About all one can say definitely as regards this experiment is that some change has taken place in the gel on conversion to sol and reconversion to gel. Addition of a little acetone or alcohol, with shaking, quickly changed the gel completely to sol, since the liquid became very mobile.

Sol rubber normally present in crude rubber is defined as that rubber which is soluble in light petroleum solvents. This rubber, as previously shown[1], originates through oxidation of the gel in latex, assisted by mechanical breakdown on the washing rolls on the estate. It can be converted to a gel through some type of vulcanization. The sol rubber resulting from the peptizing of gel with a polar solvent is a different type of sol, which reverts to gel upon removal of the polar solvent and back again to sol on addition of a polar solvent to the hexane. These observations lead to the possible conclusion that natural rubber gel is the result of strong association forces between the high-polymeric rubber molecules. This force may exist between active double bonds in certain positions, which on oxidation cause the splitting of the macromolecule and a reduction of molecular weight to the sol range, *i.e.*, less than about 200,000. After these active double bonds are satisfied by oxidation, gelation will not take place except on vulcanization with sulfur or some other agent that serves to link the sol molecules to form a gel.

The possibility that the high strength and low solubility of gel are due mainly to its high molecular weight must also be given serious consideration. This would accord with the fact that all polymers show increased strength and decreased solubility upon increased polymerization.

CONCLUSIONS

n-Hexane is shown to be an excellent solvent for fractionating sol from crude rubber and for viscosity molecular weight determinations. The instability of high-molecular rubber in tetralin and the difficulty of dispersing gel in benzene are cited as objections to these solvents for determining the average molecular weight of crude rubber.

The molecular weight calculated by the Staudinger formula:

$$M = \frac{\eta_{sp}}{C \cdot 3 \times 10^{-4}}$$

has been shown to vary with concentration to a much greater extent than the molecular weight based on the Arrhenius equation:

$$M' = \frac{\log_{10} \eta_r \cdot 10^4}{C}$$

The average molecular weight of crude rubber, determined by the viscosity method, is of questionable value on account of the insoluble gel present. The molecular weight distribution of polyprenes in crude rubber depends on the proportion of sol and gel present, which has already been shown to vary widely.

The solubility and rate of diffusion of sol into hexane from crepe rubber decrease as its molecular weight increases. Sol rubber of a molecular weight of 210,000 is practically insoluble and diffuses very slowly into hexane. The average molecular weights of sol rubber fractions from unmilled crepe range from about 60,000 to 210,000. Gel rubber has a molecular weight greater than 210,000.

Milling results in the oxidative breakdown of rubber hydrocarbon macromolecules to a much smaller but more uniform size. Hot milling results in higher average molecular weights with a different distribution than that produced by cold milling.

A polar solvent such as absolute ethyl alcohol is shown to reduce immediately the viscosity of rubber solutions in hexane. The addition of alcohol or acetone to hexane is shown to peptize gel rubber. These phenomena are explained on the basis of a reduction of association or van der Waals forces between the long-chain molecules. This peptized gel can be converted to hexane-insoluble gel by removing the peptizing agent. Swelling of rubber in an organic solvent is shown to depend on the nature of the gel present. A gel that has been peptized shows greatly increased swelling in hexane when the peptizing agent has been removed.

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SOL AND GEL IN HEVEA LATEX AND CRUDE RUBBER

INFLUENCE OF OXIDATION ON GEL-SOL TRANSFORMATION *

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From the work of Caspari[1], Feuchter[2] and others, it is now well known that a large proportion of the hydrocarbon in unmasticated crude Hevea rubber diffuses into, and is therefore soluble in, petroleum ether or ethyl ether when the rubber is covered with these solvents and allowed to stand at room temperature. This soluble form of rubber has been termed "sol," and the residue from a prolonged and repeated solvent extraction is known as the gel skeleton, which contains practically all of the protein and ash of the original rubber associated with the tough and gristly rubber hydrocarbon termed "gel." It is apparent that the terms "sol" and "gel" rubber are somewhat indefinite, as they do not refer to definite fractions or to rubber having definite physical or chemical characteristics.

From a purely colloidal viewpoint and by definition all rubber soluble by diffusion into a solvent is sol. However, we must recognize the indistinct borderline between difficultly soluble sol and almost insoluble gel.

The so-called sol rubber carefully prepared from acetone-extracted crepe by diffusion into petroleum ether forms a clear, colorless and highly elastic substance on evaporation of the solvent. It is almost pure hydrocarbon[2], since it contains less than 0.005 per cent nitrogen and 0.01 per cent ash. Its unsaturation, determined from its iodine value[3], corresponds closely to the theoretical value for $(C_5H_8=)_n$.

Up to the present time studies of sol and gel rubber have been largely qualitative and confined to crude rubber and to highly purified rubber from latex. This paper will describe a definite procedure designed to determine the proportion of sol and gel in crude rubber and in dried latex films by the use of a petroleum-ether diffusion process. The influence of oxidation on the transformation of gel to sol has been studied by the use of this method. A search of the literature indicates that this field has not been previously investigated.

EXPERIMENTAL PROCEDURE

Fresh shipments of normal ammonia-preserved latex obtained in sealed cans from two sources were studied. Latex A was shipped from the East in tank ships and drummed on arrival; latex B was shipped in drums directly from the plantation.

The solvent employed was petroleum ether, b. p. 35-58° C., and the extraction temperature ranged from 20° to 25° C. The ratio of solvent to sample was kept between 3.4 and 3.8 grams of rubber to 250 cc. of solvent. Petroleum ether is preferred to ethyl ether, since it does not contain peroxides which catalyze oxidation, and it can be worked with more conveniently. The thickness of the sample before treatment was 30 to 35 mils. In the case of thick crepes and smoked sheets the samples were cut into thin ribbons.

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The extraction was carried out in the apparatus shown in Figure 1, employing 250 cc. of fresh solvent after each period of extraction. The samples were placed in a rust-free iron basket, which fitted into the extraction chamber. At the end of each extraction period the solvent was siphoned off and evaporated to final dryness in a vacuum at 70° C.; the amount of extract was weighed. The samples were not previously extracted with acetone before treatment, since this is likely to result in oxidation of the hydrocarbon. The amount of soluble matter "resin," extracted overnight at room temperature by a mixture of 2 parts of petroleum ether and 3 parts of acetone, amounted to approximately 2.5 per cent for crepe

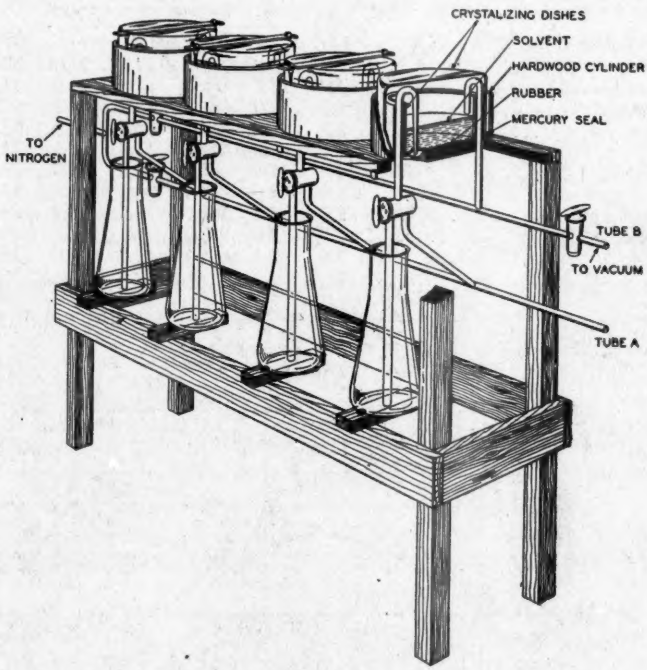

FIG. 1.—Extraction apparatus.

and sheet and for dried latex film. The samples of latex films were dried on glass over phosphorus pentoxide in nitrogen at room temperature. In the extraction process the oxygen was displaced from above the samples by nitrogen. Every precaution was observed to avoid exposure of the latex and rubber samples to light and atmospheric oxidation.

RESULTS

SOL EXTRACT IN CRUDE RUBBER

In order to standardize the method, the first experiments were carried out on crude, unmilled rubber. These results are shown in Table I, and some of the data are plotted in Figure 2.

The choice of a 72-hour extraction period is of course somewhat arbitrary. After 72 hours the rate of extraction of finely cut samples or very thin sheets

becomes very slow. If much longer periods are employed, extreme care must be taken to guard against oxidation to be certain that the added sol is not the result of oxidation. Furthermore, a portion of what we are now considering as gel may have a definite, although a low, solubility in petroleum ether.

It is seen that, in the case of crepe specimens cut from the same sheet, the extraction procedure is capable of a satisfactory degree of reproducibility of

TABLE I

EXTRACTION OF SOL FROM VARIOUS TYPES OF UNMILLED CRUDE RUBBER *

	Per cent extracted after						
Rubber	0.5 hr.	2.5 hr.	4 hr.	7 hr.	24 hr.	48 hr.	72 hr.
R.C.M.A. crepe (a) †	6.8	16.2	19.5	22.1	28.0	32.2	35.1
R.C.M.A. crepe (b) †	5.0	13.2	16.4	19.0	24.0	27.2	29.2
R.C.M.A. crepe (c) †	4.7	13.0	16.3	18.9	24.1	27.5	29.6
Water-white crepe	5.9	23.7	35.0	42.6	51.9	55.5	57.3
Yellow crepe	5.7	23.6	34.3	41.0	50.5	54.6	56.5
Purified crepe	17.2	47.8	57.4	62.2	66.6	68.5	69.2
No. 1 smoked sheet	5.9	13.8	18.8	24.1	35.4	44.5	49.0
No. 1A smoked sheet ‡	2.5	5.4	7.1	9.1	16.9	24.2	29.5
No. 1A smoked sheet §	1.0	2.5	3.0	3.6	6.8	10.2	13.2
Bolivian fine para	2.0	3.4	4.4	5.6	10.6	16.2	20.6

* The data are given as the total accumulated extract in per cent of the original sample at the end of each period.
† These samples were from the same bale. b and c were adjacent samples cut from the same sheet; a was cut from a different sheet.
‡ 33.2 per cent extract after 96 hours.
§ Uncut specimen 110 mils thick.

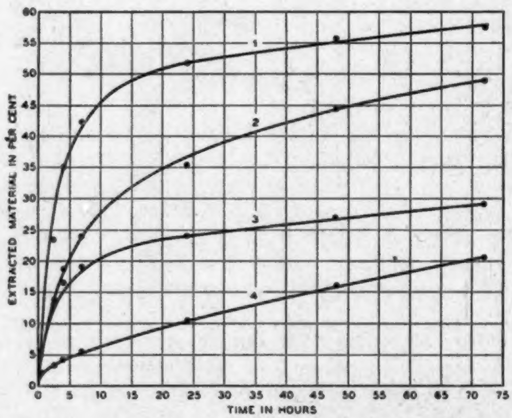

FIG. 2.—Sol rubber content in crude rubber. Curve 1, water-white crepe; curve 2, European selected smoked sheet; curve 3, R.C.M.A. crepe; curve 4, Bolivian fine para ball.

results. The effect of varying the thickness of one of the smoked sheets is to slow up the extraction considerably, and it results in a large decrease in the total extract after 72-hour extraction. The extraction is not complete after 72 hours; however, this period of time is considered sufficient to extract all but the difficultly soluble hydrocarbon. Different lots of crepe and smoked sheet were found to vary nearly 100 per cent in their content of sol rubber. The lowest value was found in the case of the Bolivian fine ball rubber. It appears that a 72-hour extraction in accordance with the above procedure is an excellent method for

determining the ratio of sol and gel in crude rubber. It is preferable to operate at a constant temperature and to cut the samples very fine to obtain the most accurate results.

Sol Rubber in Dried Latex Films

Experiments were conducted to determine the amount of sol rubber in dried rubber films from fresh shipments of ammonia-preserved latex and from the same latex exposed to oxidizing influences after receipt.

Table II

Petroleum Ether Extraction of Dried Rubber Films from Latex

Rubber	Per cent extracted after						
	0.5 hr.	2.5 hr.	4 hr.	7 hr.	24 hr.	48 hr.	72 hr.
Latex A, fresh shipment *	2.0	3.1	3.8	4.5	6.4	8.3	10.0
Latex A after moderate exposure to air †	1.8	3.1	4.2	5.0	8.3	12.5	15.9
Latex B, fresh shipment *	1.9	2.7	3.0	3.3	4.4	5.4	6.4
Latex B, fresh shipment ‡	1.7	2.6	3.4	4.0	5.6	7.2	8.5
Latex B after moderate exposure to air †	2.3	3.7	4.4	5.3	9.1	12.5	15.6
Latex B_1	1.7	2.5	2.8	3.0	4.3	4.9	5.5
Latex B_1§	0.2	0.5	0.7	0.8	1.7	2.4	3.0
Latex B film heated 2 hr. at 80° C. in air	1.8	3.1	3.7	4.4	6.2	7.7	8.7
Latex B film exposed to sunlight for 6 hours	1.7	2.5	3.0	3.4	5.1	7.5	9.6
Latex B film exposed 18 hours under G.E. sun lamp	2.2	4.8	5.8	6.9	11.1	15.9	20.6
Latex B film creped through rolls ¶	11.6	25.1	32.0	34.8	39.3	43.3	47.8

* The sample was taken on receipt. The drying and extraction were carried out in the dark and under an atmosphere of nitrogen.
† After keeping the latex for a few weeks and intermittently exposing it to the air.
‡ The sample was dried in the air and in the dark.
§ After deducting the acetone-soluble portion.
¶ Dried latex film rubber creped twelve times through even speed calender rolls until it resembled plantation crepe.

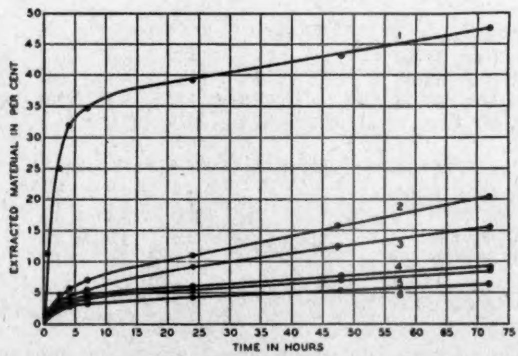

Fig. 3.—Sol rubber in dried latex films. Curve 1, film creped twelve times through rolls; curve 2, film exposed 18 hours under sun lamp; curve 3, film from latex exposed to air; curve 4, film heated 2 hours in air at 80° C.; curve 5, film from fresh latex; curve 6, film from fresh latex prepared under oxygen-free conditions.

The results presented in Table II and plotted in Figure 3 show that dried films of rubber from fresh commercial ammoniated normal latex contain only from 5.5 to 10 per cent extract after extraction for 72 hours with petroleum ether. On

exposure to air or light or when creped on rolls the content of sol rubber increases in proportion to the severity of the oxidizing treatment. After correcting for the 2.5 per cent acetone extract, the amount of sol rubber hydrocarbon from the carefully protected latex rubber ranges from 3 to 7 per cent. In other words, sol rubber appears to be a product resulting from oxidation of the gel rubber, which apparently comprises practically all of the rubber in the latex particles.

To study the effect of the thickness of the latex film, latex B_1 in a 31-mil film was compared with a finely cut 31-mil film and a 7-mil film. The results of extraction for 72 hours were 2.9, 3.3, and 4.5 per cent, respectively, after correcting for the acetone extract.

It appears that the intermittent exposure of latex to air involved in the opening of a sealed can is sufficient to cause an increase in its sol rubber content. Extra handling and exposure to air may account for the higher sol content in latex A as compared with latex B. In view of this it would be of interest to determine sol in freshly tapped latex when quickly dried out of contact with light and oxygen. An experiment of this kind, however, would have to be carried out by those having laboratory facilities near the rubber-growing areas. A study should be made of the variation in sol content in latex from trees of varying age and environment under different tapping conditions as well as of the effect of adding ammonia and storing in drums.

Effect of Different Solvents on Extraction of Rubber

Since petroleum ether varies somewhat from lot to lot, the effect of using petroleum solvents having a variation in boiling range was determined. The results of this study are given in Table III and show that small variations in

Table III

Effect of Different Petroleum Solvents on Extraction of Sol Rubber from R.C.M.A. Crepe and Dried Rubber Latex Film

Solvents employed	Per cent extracted after 0.5 hr.	2.5 hr.	4 hr.	7 hr.	24 hr.	48 hr.	72 hr.
Per cent extract of R.C.M.A. crepe							
Petroleum ether (b.p. 35–40° C.)	5.4	14.7	18.0	20.7	26.8	30.7	32.8
Petroleum ether (b.p. 35–58° C.)	5.4	14.9	18.1	20.6	26.5	30.5	32.8
Petroleum ether (b.p. 40–58° C.)	5.3	14.4	18.1	21.0	27.3	31.4	33.7
Ligroin (b.p. 80–90° C.)	5.3	20.0	27.0	31.7	38.5	43.0	45.7
Per cent extract of latex rubber film *							
Petroleum ether (b.p. 35–58° C.)	1.7	2.3	2.7	3.0	4.1	5.2	6.2
n-Hexane (b.p. 66–70° C.) †	1.8	3.0	3.4	3.8	5.2	7.3	9.2
Ligroin (b.p. 60–80° C.)	1.8	2.9	3.3	3.8	5.2	7.0	8.8
Ligroin (b.p. 80–90° C.)	1.8	3.1	3.6	4.2	6.0	7.8	9.7

* Latex B, fresh shipment.
† Skellysolve from Skelly Oil Co.

the boiling range of petroleum ether do not affect the amount of extract from R.C.M.A. crepe, whereas the use of higher boiling ligroin increases the amount of extract considerably.

The results in Table III show that a small increase in the extract from dried rubber latex films results from employing higher boiling petroleum fractions. These extracts resemble gel rubber in toughness, so that one must keep in mind that sol rubber varies from a soft state up to the tougher gel and that its solubility

becomes lower as it approaches the gel state. No sharp line of demarcation of course exists.

The use of ethyl ether and the longer extraction period employed by Pummerer, Andriessen, and Gundel[6] explains the relatively higher content of sol rubber found by them. The high sol rubber content of purified rubber from latex found by Pummerer and coworkers is readily explained on the basis that oxidation of the gel component took place as a result of the purification treatment. The results on purified crepe in Table I confirm this view. Furthermore, the purified rubber obtained by the Pummerer alkali purification process is amber in color, the color being the result of oxidation.

We have found that the sol rubber content determined by extraction with ethyl ether is higher than that found by employing petroleum ether. For example, dried latex films prepared from latex several weeks old had a 72-hour petroleum ether extract of 15.9 per cent, whereas its ether extract was 30.2 per cent when the same method of extraction was employed. It is well known that ether forms peroxides very readily, and it appears that the higher sol content found by employing ether is due to the oxidation of gel rubber to sol rubber by traces of peroxides almost always present in the ether or formed during the extraction process, owing to the fact that absolute exclusion of oxygen is not attainable.

In Figure 6 there is shown the effect of changing from petroleum ether to ethyl ether (distilled over sodium and containing 0.001 per cent of peroxide) in the extraction of a dried latex film which had been exposed to air and contained a higher content of sol than usual. The increase in rubber extract appears to be due not to an increased solubility of rubber in ethyl ether but to oxidation, since the ethyl ether-soluble fraction on removal of the ether is freely soluble in petroleum ether. The effect of extracting with ethyl containing 1 per cent of benzoyl peroxide is also shown in Figure 6.

Considerable work following that which is recorded in this paper has shown that normal hexane (Skellysolve), boiling between 66° and 70° C., is a more satisfactory solvent than petroleum ether for determining the sol rubber content. The sol content determined by the use of hexane is slightly higher than by the use of petroleum ether. The higher and narrower boiling range of hexane makes it easier and safer to handle than petroleum ether.

Treatment of Latex with Hydrogen Peroxide

Hydrogen peroxide is sometimes used to bleach dark-colored latex. At the present time no test is employed to detect whether this or other chemical additions are injurious to the rubber in the latex. Table IV gives the results of adding

Table IV

Effect of Hydrogen Peroxide on the Sol Rubber Content of Latex Rubber

Time of extraction, hours	Per cent extract with petroleum ether			
	Untreated latex *	Latex containing 0.3 per cent H_2O_2		Latex containing 3.0 per cent H_2O_2
0.5	1.7	1.6	1.9	2.0
2.5	2.3	3.0	3.2	3.7
4	2.7	3.7	3.8	4.5
7	3.0	4.4	4.5	5.5
24	4.1	6.9	6.7	9.8
48	5.2	10.8	11.0	16.4
72	6.2	14.6	14.9	24.0

* Latex B dried in nitrogen over phosphorus pentoxide.

hydrogen peroxide in 0.3 and 3.0 per cent concentrations to the latex and allowing the latex to stand 48 hours at room temperature after the hydrogen peroxide was added. It is seen that the addition of hydrogen peroxide results in a substantial increase in the sol rubber content.

Conversion of Gel to Sol Rubber by Catalytic Oxidation

The effect of adding copper and manganese salts to normal latex was studied. Copper was added as copper sulfate in concentrations of 0.1 and 0.3 per cent copper, based on the latex. Manganese in the same concentration was added as

Table V

Effect of Manganese and Copper Salts on the Conversion of Gel to Sol Rubber in Latex

Time of extraction (hours)	Untreated latex	Per cent extracted with petroleum ether: 0.1% Mn 48 hr. contact	0.1% Cu 48 hr. contact	0.1% Mn 11 days contact	0.1% Cu 11 days contact	0.3% Mn 24 hr. contact	0.3% Cu 24 hr. contact
0.5	1.7	2.3	2.2	4.7	2.5	8.6	3.1
2.5	2.3	3.9	4.0	15.3	5.3	29.1	8.6
4	2.7	4.7	5.0	23.6	7.6	45.2	12.9
7	3.0	5.6	6.4	32.6	10.7	54.4	20.0
24	4.1	8.4	11.4	46.8	20.2	61.4	37.5
48	5.2	11.1	17.0	51.7	27.1	63.5	44.5
72	6.2	13.5	22.7	53.6	32.0	65.1	48.4

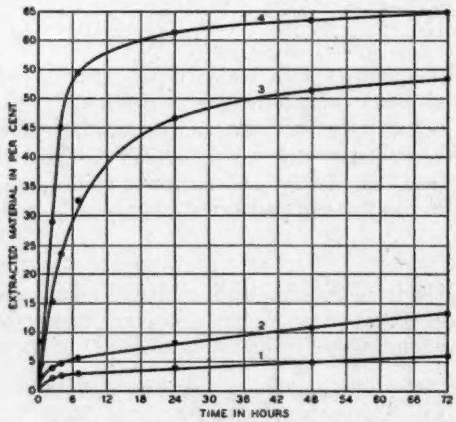

Fig. 4.—Effect of manganese on gel-sol conversion in latex. Curve 1, control; curve 2, 0.1 per cent manganese after 48 hours; curve 3, 0.1 per cent manganese after 11 days; curve 4, 0.3 per cent manganese after 24 hours.

the hydroxide. The latex was shaken from time to time over various periods, and the sol rubber content determined by the method as outlined. The results are given in Table V and plotted in Figures 4 and 5. The great activity of copper and manganese in catalyzing the conversion of gel to sol rubber by oxidation is evident. It is of interest to point out that even in the extreme cases of gel to sol conversion the latex film remained highly elastic. The sol rubber, however, in these cases was quickly converted to a viscous liquid when heated on the water bath and exposed to air, which resulted in further oxidation.

It is interesting to note that manganese in both concentrations is more active than copper, except in the lower concentration for the shortest period.

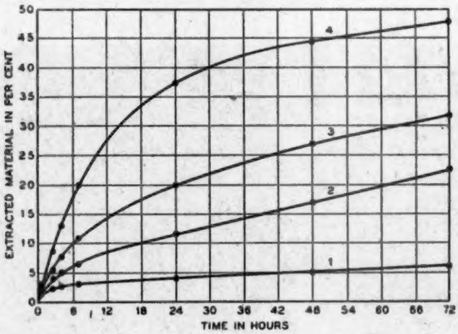

FIG. 5.—Effect of copper on gel-sol conversion in latex. Curve 1, control; curve 2, 0.1 per cent copper after 48 hours; curve 3, 0.1 per cent copper after 11 days; curve 4, 0.3 per cent copper after 24 hours.

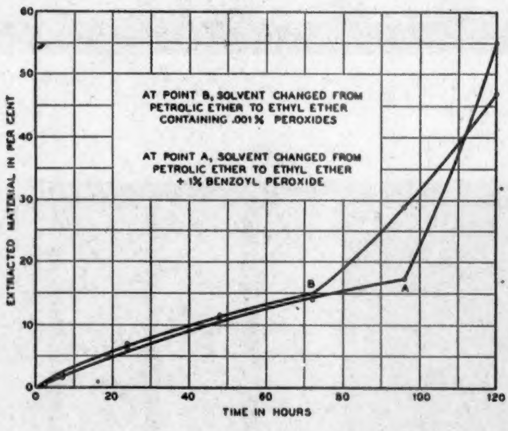

FIG. 6.—Effect of ethyl ether on sol rubber extract.

Effect of Milling

Kemp[4] has postulated that milling of rubber brings about a conversion of gel to sol rubber as a result of oxidation. The present work confirms this view.

To show the effect of milling, R.C.M.A. crepe was masticated for 5 min. on a cool laboratory mill. It was found that the total extract in 2.5 hours increases from 13.0 per cent in the unmilled crepe to 25.4 per cent after milling. Further extraction resulted in the rubber breaking up into small flocs which were unavoidably siphoned off with the solvent, thereby making it impossible to determine the amount of extract after longer periods of extraction.

The results of milling are shown better in Figures 7 and 8, taken after 1-gram cube-shaped samples of R.C.M.A. crepe from a 300-gram batch milled for various periods on a laboratory mill with cool rolls (opening 0.035 inch) were immersed in 100 cc. of petroleum ether for several days. The samples were rephotographed

after they were lightly shaken by turning the tubes end-over-end a few times and the gel aggregates were allowed to settle. The hazy appearance of the solutions after shaking is due to the finely divided proteins and salts, which do not

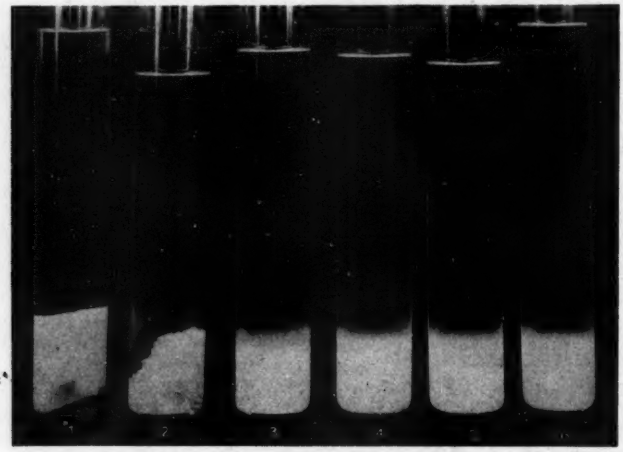

FIG. 7.—Effect of milling on gel-sol conversion. 1, unmilled R.C.M.A. crepe; 2, milled 5 min.; 3, milled 10 min.; 4, milled 20 min.; 5, milled 30 min.; 6, milled 60 min.

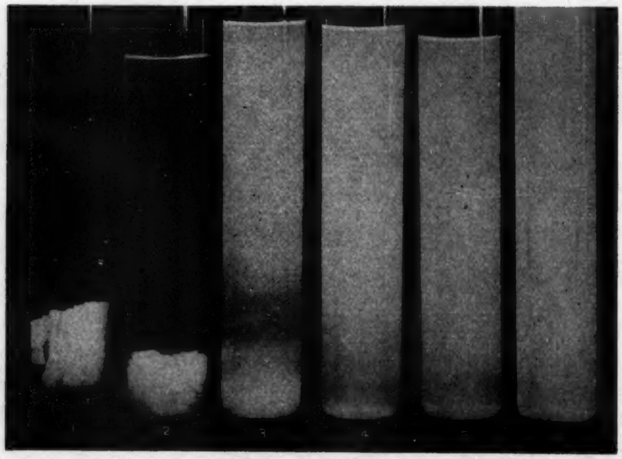

FIG. 8.—Effect of milling on gel-sol conversion. Conditions same as in Figure 7, except that the contents were lightly shaken.

settle even after several weeks standing. This demonstration clearly shows that the gel is completely converted to sol after 10 to 20 minutes of milling. Additional tests indicated that the conversion of gel to sol by milling was completed in less than 15 minutes. Continued milling probably results in a further oxidation and breakdown of the sol.

Effect of Various Solvents on Swelling

Figures 9 and 10 show the swelling of 1-gram cubes of unlimited rubbers in 100 cc. of various solvents after standing 6 days in the dark. The proximate swelling and the sol rubber extract from 1-gram cubes of dried latex film rubber after the 6-day period in 100 cc. of different solvents are shown in Table VI.

It is seen that the solubility of latex gel rubber is very low in various types of organic solvents. It is clear that the solubility and swelling of rubber depends on the nature of the rubber employed and the type of solvent used, and that one must therefore avoid generalizations in dealing with this subject. The literature on this subject is very confusing and sometimes misleading, since the nature of the rubber and the conditions of the experiments have not always been clearly

Table VI

Proximate Solubility and Swelling of Whole Latex Rubber in Various Solvents *

Solvent employed	Volume of clear solution (cc.)	Volume of swollen gel (cc.)	Swelling of gel (per cent)	Extract in clear solution † (per cent)
Petroleum ether	85	15	1500	3.4
Chloroform	82	18	1800	4.9
Benzene	76	24	2400	3.8
Carbon tetrachloride	60	40	4000	2.4
Carbon disulfide	22	78	7800	4.6

* 1 gram of rubber in 100 cc. of solvent in the dark for 6 days at room temperature.
† Shows the percentage of rubber soluble in solvents by diffusion.

Table VII

Swelling of Various Types of Rubber in Petroleum Ether

Sample	Swelling (per cent)	72-hr. sol rubber extract (per cent)
Dried latex film	1500	5.5
Bolivian fine	1000	20.6
No. 1 smoked sheet *	2400	29.5
No. 1 smoked sheet †	1300	54.8
Purified crepe	2400 ‡	69.2

* Mooney shear viscosity 92.
† Mooney shear viscosity 75.5.
‡ Loose gel structure.

defined. It is of interest to note that, although the rubber in carbon disulfide is swollen to the point where the gel is like a thick cement, the clear carbon disulfide solution free from swollen gel contains about the same amount of total diffused extract as is present in the other solvents. These observations show that gel does not diffuse appreciably into a variety of organic solvents. This fact defines rubber gel.

The swelling of 1-gram cube-shaped samples of various types of rubber[10] in petroleum ether after standing in 100 cc. of petroleum ether in the dark at room temperature for 6 days is given in Table VII, along with their 72-hour sol rubber extract. The swelling was determined by measuring the volume of the gel-free supernatant liquid and subtracting this from 100 to obtain the volume of the swollen gel, which is expressed as the increase in the volume of the original 1 cc. of rubber. It is apparent from these data that there is no relationship between the sol content and the extent of swelling.

Fig. 9.—Swelling of various types of unmilled raw rubber in petroleum ether. 1, purified crepe; 2, No. 1 smoked sheet, 75.5 Mooney shear viscosity; 3, No. 1 smoked sheet, 92 Mooney shear viscosity; 4, Bolivian fine para; 5, dried latex film.

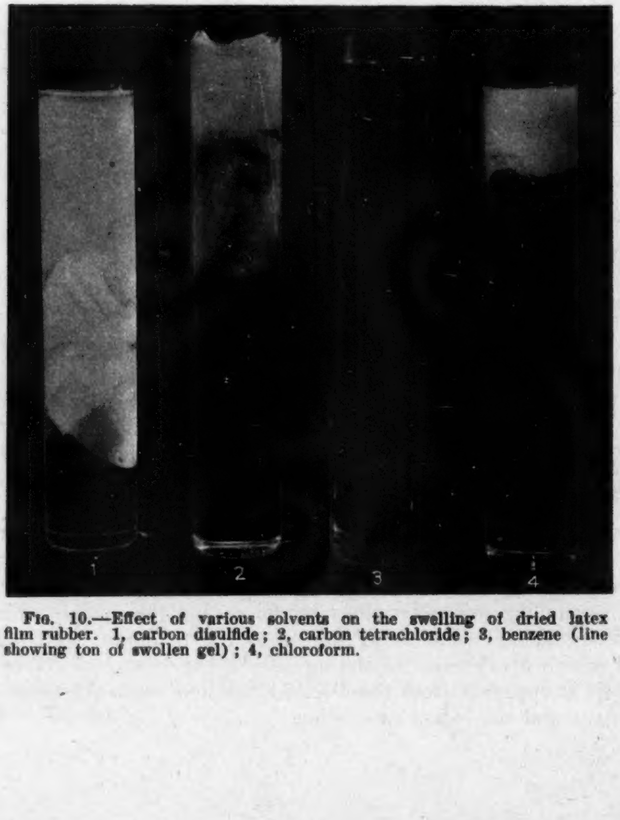

Fig. 10.—Effect of various solvents on the swelling of dried latex film rubber. 1, carbon disulfide; 2, carbon tetrachloride; 3, benzene (line showing ton of swollen gel); 4, chloroform.

The addition of 5 cc. of piperidine to the fully swollen gel in 100 cc. of petroleum ether and also in 100 cc. of benzene resulted in a considerable shrinking of the gel in both cases upon standing. This is not in agreement with the literature[8].

DISCUSSION OF RESULTS

This investigation indicates the value of the extraction method for studying the nature of the rubber in different lots of commercial latex to determine whether the conditions of preservation, storage, handling or chemical treatment have affected the hydrocarbon.

It also appears from the present work that rubber in the form of latex is very susceptible to oxidation on exposure to air, which results in an increase in its sol rubber component. It further becomes apparent that the treatment of latex and coagulum on the rubber estates in the process of making crepe and smoked sheet results in sufficient oxidation of the gel rubber in the latex particle to convert a considerable portion of it to the soluble state. Variations existing in estate practice undoubtedly account for the wide range of sol content found in crude rubber.

Rubber which diffuses into petroleum ether is considered to be a molecular dispersion. The least soluble fraction contributes the greatest increase to viscosity and has the highest molecular weight. When unmilled crude rubber is placed in a hydrocarbon solvent and shaken in the absence of oxygen, the swollen gel is broken up and dispersed into small aggregates. A molecular weight determination of such a system by viscosity measurements may be somewhat indefinite, since only the gel portion of the rubber is not likely to be molecularly dispersed.

Since sol rubber results from oxidation of gel rubber, it is quite logical to expect it to contain a small quantity of combined oxygen. The double bond present in each C_5H_8 group in the rubber polymers offers the opportunity for oxygen addition as the moloxide or peroxide. Following this addition, rupture of the chain molecule can occur, leaving oxygen combined with both fragments. If the assumption is made that one molecule of oxygen splits a rubber molecule in two equal[4] parts[11], this can be expressed by the following formula, assuming oxygen already combined at each end of the starting molecule:

$$(C_5H_8)_nO_2 + O_2 \rightarrow 2[(C_5H_8)_{\frac{n}{2}}O_2]$$

and

$$(C_5H_8)_{\frac{n}{2}}O_2 + O_2 \rightarrow 2[(C_5H_8)_{\frac{n}{4}}O_2], \text{ etc.}$$

The following oxygen contents calculated in the resulting products where n equals 10,000, 1,000, and 100 are 0.005, 0.05, and 0.5 per cent, respectively. Midgely, Henne, Shepard, and Renoll[6] found by direct determination that sol rubber contains from 0.02 to 0.04 per cent of combined oxygen, which was increased to 0.44 per cent by milling. According to the above reaction mechanism, a content of 0.04 per cent oxygen corresponds to a polymer having an average molecular weight of 80,000, which is of the same order as the average molecular weight found for sol rubber by the Staudinger viscosity method. Sol rubber oxidizes readily, and, if it reacted with 0.4 per cent additional oxygen on milling, it is not at all unlikely that its average molecular weight would be reduced from 80,000 to about 8000.

It is recognized that oxygen may play the role of a polymerization or gelling catalyst as well as a depolymerization agent. Spence and Ferry[7] have recently found that sol rubber becomes insoluble when latex is treated with quinones. They

attributed this to enhanced polymerization by linking the sol units with oxygen to form a gel.

Some investigators have considered that sol and gel hydrocarbons exist in some sort of a physical equilibrium, wherein it is possible to convert gel to sol and back again to gel. The present work shows that gel is converted to sol by an oxidation process, which ruptures the gel hydrocarbon, producing fragments of lower molecular weight, with increased solubility in organic solvents. In this case the sol might be expected to contain more combined oxygen than the gel. On the other hand, it is possible to increase the solubility of the latex gel hydrocarbon in petroleum ether by the addition of a polar solvent such as alcohol or acetone; this is probably the colloidal effect known as peptization.

The mechanism of the reaction in which oxygen reacts with the gel hydrocarbon to form sol is not known. The small combined oxygen content of sol rubber and its increase on milling, as shown by Midgley and his coworkers[5], is evidence, however, that the reaction involves addition of oxygen to the double bond, followed by splitting of the gel molecules.

It cannot be decided on the basis of present evidence whether natural gel rubber is a single high polymer chain or fiber unit or whether cross-linking bonds between the long chains or fibers exist. Primary valence bonds existing between the polymeric chains would explain the swelling of gel rubber. The micellular theory, involving associated bundles of fiber molecules held together by van der Waals forces, has also been advanced to explain swelling. More research is needed in this field to clear up the picture.

It is now clear that rubber is subject to change from the time it flows from the wound in the tree. For this reason separate investigators are likely to reach different conclusions regarding the result of experiments on various lots of rubber latex or plantation grades, since the handling and processing of these materials involves many variables which are reflected in variations in the product. Aside from the variations in content of non-hydrocarbon components in latex and plantation rubber, the present work has shown that variations as regards the state of its hydrocarbon should be given greater consideration in the future.

The prevailing conception that latex globules are made up of a semifluid sol rubber center surrounded by a tough elastic shell may be questioned in view of the present work. The sol portion in crude rubber is the product from oxidation of the latex gel and is present in an amount which depends on the extent of this oxidation. About 75 per cent of latex gel appears to be readily oxidized to sol, but the remainder requires a severe oxidative treatment such as milling to convert it to sol. This indicates that the hydrocarbon gel in latex may vary widely in molecular weight. The portion which is most difficult to break down would be expected to have the highest molecular weight.

SUMMARY

An apparatus and procedure to determine the amounts of sol and gel rubber in dried latex films and crude rubber have been described.

It is shown that whereas plantation smoked sheet and crepe contain large and varying quantities of rubber soluble in petroleum ether, dried rubber films from latex are practically free from sol rubber when oxidation has been avoided.

Latex increases in sol rubber content when subjected to various treatments permitting oxidation of the hydrocarbon. It appears from this work that the rubber in the form of latex is very susceptible to oxidation, which however involves only minute quantities of combined oxygen.

When latex film rubber is subjected to creeping, it shows an increased content of sol rubber corresponding to that of crepe. A short milling of crepe was found to convert it completely into sol rubber. This confirms the gel-sol transformation mechanism of breakdown.

Gel rubber from dried latex films is swelled to a maximum of 1500 to 7800 per cent but is not dissolved when placed in benzene, chloroform, carbon tetrachloride or carbon disulfide and allowed to stand for several days. Gel rubber becomes soluble and therefore diffusible in these solvents as a result of oxidation.

It was found that dried latex film and various types of crude rubber swelled to a maximum of 1000 to 2400 per cent in petroleum ether and that this swelling was not proportional to the sol content.

This investigation strengthens the belief that sol rubber is an oxidation product of gel rubber. The formula for sol rubber is suggested as $(C_5H_8)_nO_2$, and a relationship between the molecular weight and the oxygen content is postulated on the basis that oxygen acts as a molecular splitting agent for both gel and sol.

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[9] Midgley, Henne, Shepard and Renoll (see reference 5) found from 0.02 to 0.04 per cent of combined oxygen in sol rubber.
[10] The samples of No. 1 smoked sheet and the Mooney shear viscosity values were given us by R. H. Gerke of the United States Rubber Company, whose courtesy is hereby gratefully acknowledged.
[11] It is assumed only for convenience that the chain is split in the middle. It could, of course, be split at any double bond.

X-RAY DIFFRACTION PATTERNS OF HEVEA, MANIHOT AND OTHER RUBBERS *

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I. INTRODUCTION

The preparation of ether sol and gel fractions of rubber from *Hevea brasiliensis* was described in a previous publication[1]. When fractions prepared by that method are stretched, the sol fraction does not produce the x-ray diffraction pattern characteristic of a crystal fiber[2], but such a pattern is formed by stretched total rubber. The stretched gel fraction produces a pattern at approximately 100-per cent elongation, and at 200-per cent elongation the pattern is quite sharp and intense. Ether sol and gel fractions have not been reported to occur in all crude rubbers. They may be obtained, however, from the rubber of *Manihot glaziovii*, a tree closely related to *Hevea brasiliensis*. The ether sol and gel of *Manihot* rubber, when stretched, have been examined by x-rays for comparison with the behavior of the corresponding fractions of *Hevea* rubber.

Some years ago it was reported by Hauser[3] that twenty rubbers from different sources were found by x-ray examination to be alike. Since that time x-ray measurements have been refined. Three rubbers, other than *Hevea*, were examined by modern equipment to check Hauser's observations. In our earlier work a large spacing was noted in a specimen of unstretched *Hevea* gel rubber and, for comparison with it, a new specimen of this fraction has been investigated in the stretched condition.

II. PURIFICATION OF THE RUBBERS

The rubbers used in the present work were obtained as lactices from the nursery of the Department of Agriculture at Coconut Grove, Fla., through the courtesy of the Office of Plant Exploration and Introduction. They represented *Hevea brasiliensis, Manihot glaziovii, Funtumia elastica, Cryptostegia grandiflora* and *Castilla elastica*. Their purification was undertaken by a method which had been developed with *Hevea* latex. As originally described, it was used successfully with *Castilla* latex, and the resulting rubber contained 0.04 per cent of nitrogen. With the other latices some modification of the original method was necessary, because natural latices have differing characteristics.

Manihot glaziovii, the rubber of which is known in commerce as Ceara or Manicoba, belongs to the same family, *Euphorbiaceae,* as *Hevea brasiliensis* and has some marked resemblances to it. For example, the trees of each species may be subjected to suitable repeated tappings without a diminishing yield of latex. The latex of *Manihot glaziovii,* however, is less stable than that of *Hevea brasiliensis,* and may coagulate during tapping[4]. The *Manihot* latex as received always was coagulated. The loose coagulum was washed with successive portions

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of distilled water to remove serum components, then cut into pieces about 1 cu. mm. and again washed with water. As much protein as possible was removed by digestion with a solution of trypsin, but since the solution could not penetrate the coagulated rubber, some protein remained. The residual rubber was washed with a 1-per cent solution of sodium hydroxide at room temperature, and then with distilled water until all alkali was removed. The extracted total rubber contained 0.09 per cent of nitrogen (determined by the Kjeldahl method). Part of the nitrogen is doubtless accounted for by protein, which does not affect the diffraction pattern of stretched rubber. Finally, the rubber was extracted with acetone for 18 hours in an apparatus through which nitrogen was passed, and then extracted with ether to separate the sol form from the gel form. As an additional precaution against oxidation, some of the natural antioxidant extracted from pale crepe *Hevea* rubber was dissolved in the acetone and in the ether.

The latex of *Funtumia elastica* contains an effective stabilizing agent which inhibits coagulation. After treatment with trypsin, the latex was dialyzed to remove as many of the impurities as possible, and coagulated with acetone. The rubber was dissolved in benzene, the impurities were allowed to settle, and from the clear solution in benzene the rubber was precipitated with acetone. When benzene, acetone and moisture were removed, the rubber contained 0.07 per cent of nitrogen.

When the latex of *Cryptostegia grandiflora* was treated with trypsin, a black solid material slowly collected on the surface. It was removed and discarded. Subsequently, the latex was dialyzed, and most of the residual colored material was removed, but the rubber slowly coagulated. The coagulum was collected, washed with hot water, dried, and as much of it as possible was dissolved in benzene. When the impurities had settled, the dissolved rubber was precipitated by acetone. It contained 0.02 per cent of nitrogen. When treated with benzene or with ethyl ether, this rubber did not dissolve completely. Some undissolved gel and impurities remained.

III. MELTING TEMPERATURES OF FROZEN SPECIMENS

The melting temperatures of crystalline material in specimens of *Hevea* rubber, crystallized by "freezing" at suitable low temperatures, have already been reported in this journal[5]. The temperatures within which melting occurred were not the same for all the specimens, but all melted between —5° and +16° C. This range was similar to that previously observed with discrete crystals prepared from ethereal solutions. For comparison with these observations, the melting ranges were determined of frozen specimens prepared from the other latices used in this work. As was observed with *Hevea* rubber, the temperatures of melting with different specimens of the same rubber were not alike, but specimens of all the rubbers melted within the range $-5°$ to $+16°$ C.

IV. X-RAY PATTERNS

Except when otherwise indicated, the technique used for x-ray measurement is the same as that which was described in a previous publication[6].

The specimens of *Manihot* sol and gel with which patterns were obtained were stretched quickly, almost to the breaking point. In Figure 1 (*A*) that of the sol is reproduced and in Figure 1 (*B*) that of the gel. Each pattern was made with filtered $K\alpha$ radiation from copper. The pattern of the sol definitely shows less perfect fibering. A monochromatic fiber pattern of stretched *Manihot* gel is shown

in Figure 1 (C). The monochromatic beam was obtained by diffracting the x radiation from copper from the ground surface of a crystal of pentaerythritol, according to the technique described by Fankuchen[7].

A list of the more important measurements obtained with stretched *Manihot* gel is given in Table I. The deviations of spacing from the corresponding measurements with *Hevea* gel rubber are doubtless caused by an uncertainty in estimating

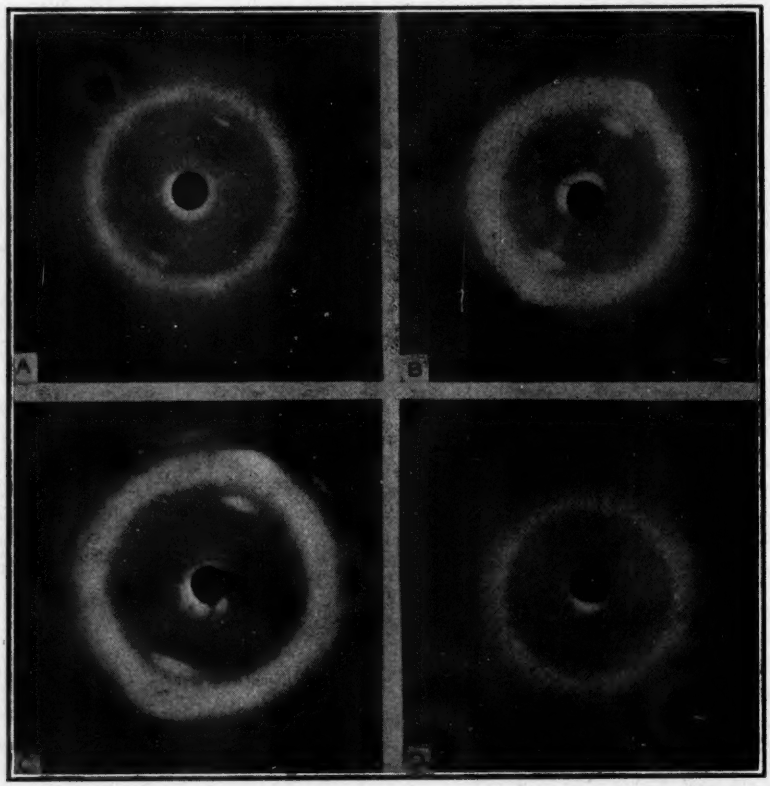

FIG. 1.—X-ray diffraction patterns.

A and *B* were obtained with stretched *Manihot* sol and gel rubbers, respectively, made with filtered $K\alpha$ radiation from copper; *C* is a monochromatic fiber pattern of stretched *Manihot* gel; and *D* is a pattern of frozen *Manihot* gel.

the center of the stretched sample. The distance from specimen to film was about 6.9 cm.

Specimens of unstretched *Manihot* sol and gel were kept simultaneously at −20° C. for 24 hours. Two interferences were observed with the sol fraction, corresponding to spacings of 6.18 A and 4.25 A.

The pattern shown in Figure 1 (D) is that of the frozen *Manihot* gel. It was made in a low-temperature camera very similar to that used by Wolthuis[8], but with less distance, approximately 3 cm., between specimen and film. The exact distance was determined by calibration with sodium chloride. Unfiltered $K\alpha$ radiation from copper was used. Measurements of the pattern are given in

Table II with the computed interplanar distances, which are compared with those previously found for frozen *Hevea* gel rubber[9].

Hauser[10] examined with x-rays rubbers from twenty different sources. The rubbers represented different botanical classifications and came from different geographical origins. The lattice spacings and intensitives were the same in all. Since that work was done, the methods of producing x-ray diffraction patterns

TABLE I

MEASUREMENTS FROM STRETCHED MANIHOT GEL RUBBER

[In the tables, d is the distance between the set of planes making an angle θ with the incident beam, R is the radius of the diffraction spot or ring as measured on a flat film and the letter i indicates an intense interference.]

Designation of lines	Radius, R (cm.)	d (A)
Equatorial layer line:		
A1	1.69i	6.28
A2	2.62i	4.26
A3	3.70	3.16
First layer line:		
B1	2.20i	5.02
B2	2.99i	3.79
B3	3.31	3.49
Second layer line:		
C0	2.72	4.12
C1	3.32i	3.46
C2	3.86	3.05

TABLE II

MEASUREMENTS FROM FROZEN MANIHOT GEL RUBBER AND THOSE PREVIOUSLY OBTAINED FROM FROZEN HEVEA GEL RUBBER

Lines	*Manihot* gel Radius cm.)	*Manihot* gel d (A)	*Hevea* gel d (A)
1	0.67	6.30	6.20
2	.86	5.02	4.99
3	1.04	4.21	4.20
4	1.18	3.76	3.74
5	1.25	3.58	3.48
6	1.31	3.44	—
7	1.37	3.31	—
8	1.42	3.21	—
9	1.53	3.02	3.02
10	1.61	2.89	2.82
11	2.58	2.07	2.07
12	2.69	2.02	—

have been much improved and, at present, measurements of rubber by different investigators agree within a few hundredths of an angstrom unit.

X-ray measurements were also made on frozen specimens of *Funtumia elastica, Cryptostegia grandiflora* and *Castilla elastica.* The values of interferences obtained with each rubber agreed and were the same as those reported by Lotmar and Meyer[11], by Clark, Wolthuis and Smith[12] and by Barnes[13] within 0.05 A. These results confirm the earlier observations of Hauser.

In a previous publication[14] there was an illustration of a long spacing of 54 A, which was observed in a specimen of unstretched ether gel of *Hevea* rubber. The spacing was absent from the corresponding sol. The gel from which the specimen was taken was stored in contact with ether and in darkness at temperatures between 2° and 6° C. to suppress oxidation. It was hoped that during storage, any residual soluble material would be dissolved, leaving undissolved the molecules of greatest weight. Under the conditions of storage, however, less than 2 per cent of the gel became soluble. After 18 months a specimen was freed of ether and it was examined by x-rays. The diffraction pattern of the stretched material, using filtered $K\alpha$ radiation from copper, is reproduced in Figure 2. The same long

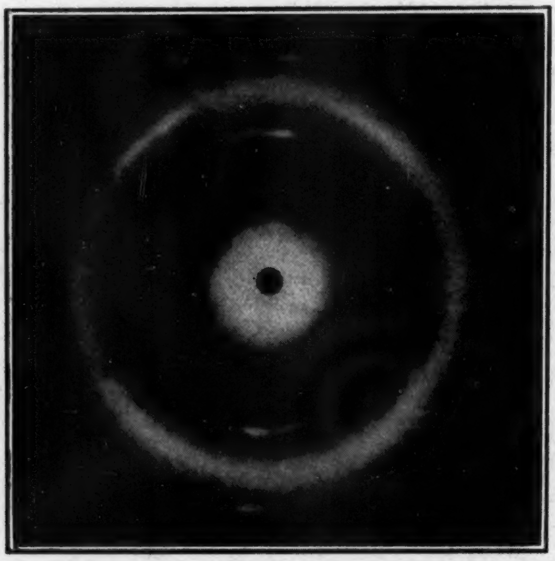

FIG. 2.—X-ray diffraction fiber pattern of stretched *Hevea* gel rubber, showing two large interplanar spacings.

spacing appears at the position observed before, 54 A. The long-spacing arcs on the equator of the pattern are clearly visible. In addition there is faint but definite evidence of a second still longer spacing which corresponds to about 108 A. On the film this ring appears as a darkened area around the central spot.

SUMMARY

When rubber from *Hevea brasiliensis* is stretched quickly and exposed to a beam of x-rays, a crystal fiber diffraction pattern is obtained. During previous work, done jointly by the National Bureau of Standards and the University of Illinois on sol and gel fractions of this rubber, no pattern was produced by the stretched sol fraction. With the stretched gel fraction, however, the pattern was sharp and intense. Rubber from *Manihot glaziovii* also may be separated into sol and gel fractions, and in recent work they, too, have been stretched and examined by x-rays. With the stretched *Manihot* sol, a few interferences were obtained, but many more resulted with the stretched gel. When crystallized by "freezing" at low temperatures for 24 hours, the interferences from the gel again

outnumbered those from the sol. The x-ray measurements of *Manihot* rubber agree with those of *Hevea* rubber and indicate that the same structure exists in each. Rubbers obtained from latices of *Funtumia elastica, Cryptostegia grandiflora* and *Castilla elastica* were also examined. Their structures, too, were like that of *Hevea* rubber, and the similarity confirms earlier observations made when x-ray technique was less highly developed. In crystallized specimens, the crystals melted within the range of temperatures previously observed with *Hevea* rubber.

In earlier work a large spacing was observed in a specimen of unstretched *Hevea* gel rubber. This spacing has been observed also in a new specimen of stretched *Hevea* gel rubber, together with a second spacing approximately twice as large.

ACKNOWLEDGMENT

The material used in this work was obtained from the Department of Agriculture through L. G. Polhamus, Bureau of Plant Industry, Washington, D. C., and H. F. Loomis, U. S. Plant Introduction Garden, Coconut Grove, Fla. Their coöperation is appreciated.

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THE CRYSTALLIZATION OF WEAKLY VULCANIZED RUBBER BY PRESSURE *

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Crystallization can be brought about in weakly vulcanized rubber by the method described by Thiessen and Kirsch[1] for natural rubber. When samples of this type of vulcanized rubber were exposed to x-rays below +6° C., but not under pressure, then Debye-Scherrer diagrams corresponding to those of a crystallized latex film were obtained.

To determine the influence of pressure on these vulcanizates, samples were subjected to pressure on all sides in the chambers of the pressure apparatus described in the earlier work. After having been exposed for 100 days the sample which had been kept at +6° C. under 30 atmospheres' pressure showed a very marked Debye-Scherrer diagram, whereas samples kept at the same temperature but at normal pressure showed only the halo of an amorphous substance. Consequently pressure has an influence on the crystallization of vulcanized rubber as well as of raw rubber. The melting point of the crystalline phase lies between +11° C. and +13° C. Obviously then an increase in pressure raises the temperature range of supercooling.

Samples of the same kind kept under 30 atmospheres' pressure could not be crystallized at +8° C. A more highly vulcanized rubber could not be crystallized by keeping under 46 atmospheres' pressure at −2° C. Likewise samples of commercial Oppanol B, Oppanol C, Buna and Acronal did not crystallize under 46 atmospheres' pressure at −2° C. To bring about crystallization in such experiments, still lower temperatures and higher pressures would probably have to be employed. An experimental study of this is in progress at the present time.

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* Translated for Rubber Chemistry and Technology from *Die Naturwissenschaften*, Vol. 27, No. 22, page 390, June 2, 1939.

THE JOULE EFFECT

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With reference to a paper by Gleichentheil and Neumann[1] on "The Gough-Joule Effect in Vulcanizates," we should like to call attention to the similarity between the results reported in their paper and the earlier work reported by Wiegand and Snyder[2] entitled "The Rubber Pendulum, the Joule Effect and the Dynamic Stress-Strain Curve."

The latter authors analyzed from a thermodynamic point of view the rubber stress-strain curve as affected by temperature. As a result of this analysis the stress-strain curve was divided into three groups, Region A, Region B and Region C. Each region was characterized by different trends as regards the Joule effect and internal energy changes.

The following description is taken from the original paper:

"*Region A, The Steel Spring*.—This region, extending to approximately 300 per cent elongation for the conditions in the experiments described, is characterized by the comparative absence of heat transfers . . . . little or no Joule effect."

"*Region B, The Gas (and the Crystal)*.—In region B the region of the Joule effect . . . . there is the maximum of heat evolution.

It should be noted that Region B extends from approximately 300 per cent elongation to 700 per cent elongation.

"*Region C, The Friction Member*.—This region is characterized by the almost entire absence of reversible effects. The Joule effect has disappeared. There is no evolution of heat . . . ."

Gleichentheil and Neumann show that up to 350 per cent elongation there is very little heat evolution. This corresponds to Region A of the stress-strain curve.

From 350 to 500 per cent elongation Gleichentheil and Neumann found an increased rate of heat development, and from 500 to 700 per cent a maximum rate of heat evolution. This corresponds to Region B of the curve.

Above 700 per cent elongation the heat evolution was greatly reduced, thus conforming to Region C of the paper mentioned.

In other words, the calorimetric data of Gleichentheil and Neumann confirmed the thermodynamic deductions of Wiegand and Snyder.

The above is presented with the thought that the correspondence of the two sets of data might be of interest to those engaged in the theoretical analysis of rubber behavior.

In a comprehensive discussion of the Joule effect, Vogt[3] recalculated the data presented by Meyer and Ferri,[4] and pointed out that the work of these authors confirmed the thermodynamic deductions of Wiegand and Snyder.

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VULCANIZATION OF RUBBER *

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Charles Goodyear, a hundred years ago, saved the rubber industry and made available for human needs and satisfaction a material of unique and useful properties. In the 1830's the industry was in bad straits. People wanted its products, but unfortunately the rubber of which they were made became soft and sticky in summer and stiff and inelastic in winter, and also deteriorated rapidly. Through several years of all kinds of difficulties Goodyear persisted in his idea that he could find a method of preserving the good properties of crude rubber and finally discovered not only how to preserve but also how to enhance them. Sulfur and heat gave him his answer. Sulfur and heat also formed the basis of the name "vulcanization" by which the process has been known. It was given by Brockedon, a friend of Thomas Hancock, who was the famous English pioneer in the rubber industry, a contemporary of Goodyear, and rediscoverer of the method of vulcanization.

Goodyear's method was the result of much painstaking effort, although as with all important discoveries it really is quite simple. He knew nothing of and was not required to use organic accelerators, accelerator activators, accelerator retarders, antioxidants, antiflex-cracking agents, reinforcing materials, reclaim, plasticizers, stiffeners, odorants, blowing agents, rubber substitutes, etc. However, he had plenty of headaches in getting his process into action, not only from the technical but also from the business angle. People were disgusted with rubber products and the companies which manufactured them, and he had to overcome much prejudice and antagonism.

His process has an unusual record since, even now, a century afterwards, it is still the basis of the rubber industry. This statement does not mean that there have been no advances. The very length of the list of different types of materials given above for use with sulfur in rubber indicates the extent of some of the technical advances which have been made. Also, other important advances have been made in the apparatus used in the factory and in the methods of testing the products. Goodyear tacked his sheets of rubber on the outside of his house or hung his products from the rafters of a barn to find out the effect of cold and heat. Later men used their teeth and trained their bite to gage and compare tensile strengths. But these simple and useful methods have long since been displaced by the accurate methods of the modern testing laboratory, which produce results that can be evaluated by anyone skilled in rubber work.

PROPERTIES OF VULCANIZED RUBBER

Vulcanization involves both physical and chemical changes. The most important physical change from raw to vulcanized rubber is in the plasticity. Properly vulcanized rubber is very elastic like raw rubber but, unlike raw rubber, after having been stretched it rapidly retracts almost to its original shape. In other words, it shows no apparent set. This retraction is the same at 0° C. and at lower

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temperatures where stretched raw rubber is frozen and remains stretched after the force has been removed. However, at very low temperatures, for example, −40° C., even stretched vulcanized rubber remains stretched. Both types retract as the temperature rises. This phenomenon is shown by both raw and vulcanized rubber, the difference lying only in the range of temperatures. The T-50 test[24] utilizes this fact, T-50 being the temperature at which a piece of stretched frozen rubber retracts to 50 per cent of its stretched length. In hot water raw rubber becomes soft and tears easily, but vulcanized rubber remains apparently unchanged. Thus, the outstanding characteristic of vulcanized rubber is its resistance to flow under a wide variety of conditions[22].

On a mill, vulcanized rubber is rapidly ground to nontacky shreds, whereas raw rubber soon becomes a soft tacky coherent mass. Vulcanized rubber shows greater tensile strength, usually greater elongation, less hysteresis and greater resistance to the action of solvents and heat, to tear and abrasion.

Furthermore some of the sulfur is always chemically combined with the rubber. These changes are found to varying degrees in all vulcanizates, and therefore it is difficult to cover them all in a short definition. Experimentally, a group of tests is necessary to show that a rubber compound has been properly vulcanized[21, 22, 23].

SULFUR VULCANIZATION

Vulcanization can be carried out by mixing 5 to 8 parts of sulfur into 100 parts of rubber and heating the mixture for 3 to 4 hours at about 141° C. Modern methods involve the use of organic accelerators, which shorten the time of vulcanization and give valuable properties to the products not obtainable otherwise. With a small proportion of one of these very active types of accelerators, vulcanization is complete in as many minutes as it takes hours with sulfur alone and at lower temperatures. Using these very active or ultra-accelerators, rubber can be vulcanized even at room temperature. Much smaller proportions of sulfur are required in conjunction with accelerators, and these lower proportions give desirable properties.

As the proportion of sulfur is increased to 14-18 parts, the vulcanizates have lower tensile strength and generally are not of commercial importance; but as the proportion is increased to 30-50 parts, the products become hard, the elongation drops to a very low figure, and the tensile strength increases considerably. Thus hard rubber or ebonite is made.

NONSULFUR VULCANIZING AGENTS

Under this heading all vulcanizing agents other than elemental sulfur will be considered.

Sulfur Monochloride.—The first agent other than sulfur was discovered only a short time after Goodyear's discovery. Sulfur monochloride[42] vulcanizes rubber rapidly and at room temperature, but can be used only on thin sheets of rubber.

Selenium can also be used but only in combination with an organic accelerator[8, 55]. Apparently it does not form a hard rubber. With sulfur it seems to act as an accelerator. Tellurium has little effect alone as a vulcanizing agent, although it has some value in rubber compounding.

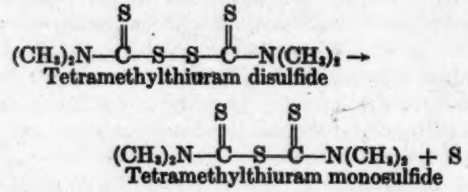
Ethyl Thiosulfite, $(C_2H_5O)_2S_2$, vulcanizes rubber at room temperature[53].

Nitrogen Sulfide, N_4S_4, an unstable substance, vulcanizes rubber[53].

Sulfur Dithiocyanate, $S(CNS)_2$, is claimed to give vulcanizates of greater durability than those obtained with sulfur monochloride[33]. A mixture of the

di- with the monothiocyanate is used in carbon disulfide, since the dithiocyanate is not very soluble.

TETRAALKYLTHIURAM DISULFIDES give very good vulcanizates, alone and in the presence of zinc oxide[4, 12]. They are also powerful accelerators of sulfur vulcanization. During vulcanization, tetramethylthiuram disulfide is reduced to the monosulfide, which blooms out, and it is believed by some that the extra atom of sulfur is split off in an active form which is said to be the real vulcanizing agent.


Tetramethylthiuram disulfide
Tetramethylthiuram monosulfide

The monosulfide is a strong accelerator but is not a vulcanizing agent, even in the presence of an oxidizing agent.

POLYNITROBENZENES were the first strictly nonsulfur vulcanizing agents. They were discovered in 1915 by Ostromislensky[40] who chose them "because, as weak oxidizing agents, they possess, like sulfur, the ability to combine with certain unsaturated hydrocarbons; in addition, many physical properties of nitro compounds, especially their existence in the form of so-called crystal isomers (polymorphism), made them resemble sulfur even more closely," also "because oxygen as an element belongs to the sulfur group." Inorganic oxides, especially litharge, are necessary for the best action of the polynitrobenzenes, and moisture is an excellent accelerator or accessory agent[57, 58]. These nitro compounds, or products derived from them, add chemically to the rubber, since the nitrogen content of the acetone-extracted vulcanizates increases with the time of vulcanization, and the unsaturation decreases[5, 51].

At least part of the polynitrobenzene is reduced, and some oxidation also takes place during vulcanization; for example, *m*-dinitrobenzene is reduced in part to what appears to be dinitroazobenzene and dinitroazoxybenzene[58].

Hard rubber types can be obtained with large proportions of a polynitrobenzene and litharge and a small proportion of water[58].

BENZOYL PEROXIDE.—The vulcanizing action of this substance was also discovered by Ostromislensky[41]. It is very active, but the vulcanizates do not age well. The vulcanizates contain benzoyl peroxide in chemical combination[5, 46]. Van Rossem[46] showed that one-third of the reagent is extractable as benzoic acid and one-third as potassium benzoate after treatment with alcoholic potassium hydroxide. Van Rossem postulates that benzoyl peroxide may act as a hydrogen acceptor, and that two molecules of the rubber hydrocarbon may thus be united at the places where the hydrogens are lost. The unsaturation of the vulcanizate decreases as vulcanization progresses[5]. In the discussion of van Rossem's paper, Bock[6] showed that, by using equimolecular portions of rubber (calculated as C_5H_8) and benzoyl peroxide, a hard insoluble product is formed.

DIAZOAMINOBENZENE AND ITS DERIVATIVES.—Buizov[13] reported the use of diazoaminobenzene as a vulcanizing agent in 1921, but the long abstract of his article in *Chemical Abstracts* does not mention the fact. Its use was rediscovered later by Levi[34] and Fisher[17]. These agents do not require the presence of any other substance, and they give clear transparent vulcanizates, some of which age well. A gas which is probably nitrogen is given off during the reaction and some-

times makes the products porous. 2,4,6,2′,4′,6′-Hexachlorodiazoaminobenzene gives excellent products, which are transparent like molded pale crepe. In this case part of the reagent was found by Shinkle and Fisher[19] to have been converted into the corresponding hexachlorodiphenylamine. The formation of this substance and of the gaseous nitrogen indicate that an oxidation-reduction takes place during the vulcanization. At the same time part of the agent evidently adds in some form to the rubber hydrocarbon, since the vulcanizate contains more nitrogen than is found in the original crude rubber[19]. The hydrogen atom on the diazoamino group, $-N=N-NH-$, is not the point of action, since compounds in which it is replaced by a methyl or a benzyl group work even better than the unsubstituted parent substance. *N*-Benzyldiazoaminobenzene has some of the properties of an ideal nonsulfur agent, since not only is it a good vulcanizing agent, but it is also its own accelerator and antioxidant.

Quinones and Halogenated Quinones were found by the writer[18, 19] to vulcanize rubber at 141° C. and, in the case of the halogenated quinones, also at room temperature. During vulcanization, a portion of the quinone is reduced to the hydroquinone, which blooms out. In the case of the halogenated quinones, it was found that a portion of the agent adds in some fashion to the rubber hydrocarbon. Spence and Ferry[48] reported that quinone and tetrachloroquinone produce "enhanced polymerization" of the rubber in latex, especially under irradiation. All the quinones give much better results in the presence of oxidizing agents such as lead dioxide, red lead, ferric oxide, mercuric oxide (yellow), and lead chromate. Large proportions of tetrachloroquinone in rubber form products which are hard and brittle. Theoretical considerations of the action of the quinones are given below.

Quinone Mono- and Diimines.—These types, especially their *N*-aryl derivatives, were discovered by the writer[17] to vulcanize rubber similarly to the quinones and also to give much better results in the presence of oxidizing agents. Spence and Ferry[48] mention quinonediimine as giving enhanced polymerization. The *N*-aryl derivatives are generally red and are at least partly reduced to the corresponding *p*-hydroxydiarylamines and *N*,*N*^{1}-diaryl-*p*-phenylenediamines, which are white and bloom out. These vulcanizates age very well.

Quinone Mono- and *bis*-Haloimines.—These substances are very active vulcanizing agents[17]. On account of their activity, vulcanization takes place sometimes on the mill or while the specimens are awaiting their turn at the press. Quinone dichlorodiimine is also mentioned by Spence and Ferry[48].

Quinone Mono- and Dioximes[17].—Quinone monoxime is a tautomeric form of *p*-nitrosophenol and works best in the presence of oxidizing agents. Quinone dioxime gives good vulcanizates alone but works best in the presence of oxidizing agents, and its activity is increased by a great many different kinds of oxidizing agents. It also adds in some way to the rubber hydrocarbon since the vulcanizates contain more nitrogen than that in the original crude rubber[19]. The methyl ethers of both quinone mono- and dioxime act even better as vulcanizing agents than the parent substances.

Substances Which Require the Presence of Oxidizing Agents.—Many of the substances which vulcanize rubber only in the presence of oxidizing agents are related to the quinones and their nitrogen derivatives discussed above. The work on some of them has been patented[17, 18], but much of it has not yet been published by the writer. The oxidizing agents which give the best results are lead dioxide, yellow mercuric oxide, manganese dioxide, vanadium pentoxide and lead chromate. Sometimes all of them give good results with the same compound,

but occasionally one gives much better results than any of the others. The organic substances are listed, and only the chief members tried are included. Their theoretical implications will be discussed later.

Dihydric Phenols.—Hydroquinone, and its halogenated derivatives, resorcinol, catechol, 4,4′-dihydroxydiphenyl.

Monohydric Phenols.—Phenol and the cresols, their halogenated derivatives, mesitol, pentamethylphenol, and the naphthols.

Mercaptans.—*p*-Thiocresol, thio-β-naphthol or β-naphthyl mercaptan, and mercaptobenzothiazole.

Phenolic Derivatives.—*p*-Hydroxydiphenylamine, *p*-hydroxyazobenzene, *p*-benzylaminophenol, *p*-benzalaminophenol.

Di-sec-Aromatic Amines.—*N,N′*-Diphenyl-*p*-phenylenediamine, 1,3,5,-trianilinobenzene, *N,N′*-diphenylbenzidine and 5,5-dimethylacridan.

Primary Aromatic Amines.—Aniline, the toluidines, mesidine, pentamethylaniline, *m*-nitraniline, the naphthylamines and *p*-aminoazobenzene.

Secondary Aromatic Amines.—Diphenylamine, phenyl-α-naphthylamine, phenyl-β-naphthylamine, benzeneazodiphenylamine.

Grignard Reagents and Zinc Alkyls.—The vulcanizing activity of these substances was demonstrated by Midgley, Henne, and Shepard[36], who showed that they acted only when the rubber hydrocarbon contained a trace of chemically combined oxygen. Tensile strengths of 135 to 160 kg. per sq. cm. (1925 to 2275 pounds per square inch) were obtained. The Grignard vulcanization can be reversed and the recovered rubber revulcanized with a Grignard reagent (the first and only instance ever reported of a complete devulcanization). Apparently no attempt has been made to vulcanize this recovered rubber with sulfur and compare its properties with other sulfur vulcanizates from natural rubber.

N,N′-Dichloroazodicarbonamidine ("Azochloramide") belongs to the aliphatic group and has the following structural formula:

$$\begin{array}{ccccccccc} Cl- & N= & C & -N=N- & C & =N- & Cl \\ & & | & & | & & \\ & & NH_2 & & NH_2 & & \end{array}$$

A mixture of 5 parts in 100 of pale crepe was found[19] to give the following results in a press at 141° C.:

Time (Min.)	Tensile strength (Kg. per sq. cm.)	(Lb. per sq. in.)	Set [a] (Inch)	Elongation (%)
15	39	(554)	0.21	910
90	46	(648)	0.21	920
150	72	(1025)	0.18	910

[a] The set is the difference between the length of an original one-inch section before and just after break.

All the samples were porous, probably from nitrogen gas formed during the vulcanization. It is of interest to compare the structure of this reagent with that of the quinone dichloroimines mentioned above.

Inorganic Vulcanizing Agents.—The writer frequently found that fairly good vulcanizates were obtained with some substances in the presence of yellow mercuric oxide. They bore such a resemblance to one another that it was thought the oxide might be the actual agent; therefore it was tried by itself. The results showed that mercuric oxide is a vulcanizing agent, and that its action is increased in the presence of stearic and other acids.

Lead dioxide is a proöxygen and gives very sticky samples but, when properly handled and heated in a press for 180 minutes at 141° C., a mix containing 30 parts of lead dioxide gives a product which is sticky but by hand tests has certain characteristics of a vulcanizate. In benzene a sample swelled and showed no signs of dissolving after 4 days, but 3 weeks later it was completely dispersed. Perhaps this is a borderline case.

Selenium dioxide has a peculiar action on rubber which may be akin to vulcanization.

Potassium ferricyanide, and to a lesser extent, mercuric chloride, ferric chloride and pentamminocarbonatocobaltic nitrate, showed enhanced polymerization of rubber in a specially prepared latex when heated in the absence of air[49].

THEORIES OF NONSULFUR VULCANIZATION

The vulcanizates prepared with nonsulfur agents are so similar to those obtained with elemental sulfur that by simple inspection it is practically impossible to differentiate them. The range of their properties is great just as the range of the properties of sulfur vulcanizates is great. Some types of agents give a wide range of properties, some a narrow range; some give strong products, some weak; some give typical T-50 tests, and some do not.

The proportions of many of the nonsulfur agents required for vulcanization are similar to those of sulfur, provided the molecular size of the agent is taken into account. For example, 4 parts of tetrachloroquinone on 100 of rubber give excellent results alone, but especially in the presence of lead dioxide. Since the molecular weight of tetrachloroquinone is 246, this amount would correspond to 0.52 part of sulfur. Only 1 part with an oxidizing agent gives a good vulcanizate and this small amount corresponds to only 0.13 part of sulfur. Also 1 part of 2,6-dichloroquinone-4-chloroimine with 2 parts of lead dioxide gives a vulcanizate with a tensile strength of 76.5 kg. per sq. cm. (1088 pounds per square inch), and this 1 part corresponds to 0.15 part of sulfur. Similar figures could be shown for other agents. These amounts are close to Bruni's calculated figure of 0.15 for approximately the lowest proportion of combined sulfur possible to give definite vulcanization.

Since all the vulcanizates have so much in common, it is likely that the vulcanization reaction is fundamentally the same. A complete theoretical explanation of the action of sulfur has not yet been put forth, and it is impossible at present to explain the action of the nonsulfur agents. However, theories are worth using since they help us to understand natural phenomena and act as guides for further research. Good as our present theories may be, they must be changed when it is necessary in order to interpret new facts properly.

Several important generalizations can be made regarding nonsulfur vulcanization.

1. Most of the agents are oxidizing agents in the broad meaning of the term.
2. Those that are not oxidizing agents require the presence of an oxidizing agent.
3. All combine chemically in some unknown form with rubber hydrocarbon.
4. The unsaturation of rubber hydrocarbon decreases as the chemical combination of the agent increases, wherever such studies have been made.
5. From observation only, it appears that all the groups which combine with rubber hydrocarbon are or contain polar groups.
6. It is not necessary to have either sulfur or oxygen in the organic molecule in order to have a vulcanizing agent.
7. The fundamental action which is common to all vulcanization is oxidation-reduction.

As will be shown later, these generalizations agree nicely with those for the chemistry of sulfur vulcanization. In discussing the theory of the action of some of these agents and its development, we will start with the quinones, since they were the first group studied by the writer.

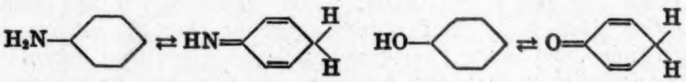
At first it was thought that the quinones added to the rubber or that the rubber added to the quinones, as hydrocarbons are known to do, and that the reaction was completed by the oxidizing action of an unreacted portion of the quinone which is thus reduced to the corresponding hydroquinone. If another oxidizing agent was present—for example, lead dioxide—it was thought that this reoxidized the hydroquinone back to the quinone which, in turn, reacted with the rubber. It happened, however, that the vulcanizates containing the lead dioxide were always much better than those without it. Also the quinones studied in the early work were the halogenated quinones, especially tetrachloroquinone (chloranil), and this substance is insoluble in rubber whereas the corresponding tetrachlorohydroquinone is soluble and blooms out. The simple vulcanizates always showed the bloom of tetrachlorohydroquinone, but the lead dioxide mixtures, provided there was enough lead dioxide present, did not. This fact was interpreted as indicating that all the hydroquinone was completely reoxidized to the quinone. It was also found that mixing tetrachlorohydroquinone itself in rubber along with lead dioxide gave excellent vulcanizates. Later work showed that red lead could replace lead dioxide with tetrachloroquinone but that it could not replace it with tetrachlorohydroquinone. No bloom was obtained also when red lead was used. Lead dioxide will oxidize tetrachlorohydroquinone outside of rubber to tetrachloroquinone but red lead will not. However, red lead will form a salt with tetrachlorohydroquinone which is insoluble in the rubber, and therefore it will not bloom out. These facts indicate that the reaction may be chiefly between the rubber and the hydroquinone, and that the chemical combination thus formed is then oxidized to what we know as the vulcanizate by the action of an oxidizing agent. The question then comes up, how does the quinone vulcanize rubber? It is probably first reduced to the hydroquinone by the reducing action of nonrubber components and rubber hydrocarbon, and then the action goes on as just given.

The rather thorough study of this reaction apparently settled the mechanism of the reaction, and work with other substances seemed to bear out these conclusions—namely, that the reduced form of the substance, provided there are two such related forms, reacts with the rubber, probably adding to it at double bonds, and then this addition product is oxidized to give the vulcanizate. Just what this final form is chemically has not yet been determined. It is a difficult problem but no doubt it will be solved one of these days.

Besides the oxygen derivatives, several types of nitrogen derivatives related to quinone (quinonimines) work satisfactorily under the same general conditions, and the chemical reaction is probably the same. Many of the oxygen and nitrogen derivatives are very active and will vulcanize rubber at room temperature, some even on the mill.

Not only did all the halogen derivatives of quinone tried give very good results, but also the simple quinones, including certain naphthoquinones. Hydroquinone, with an oxidizing agent, vulcanized rubber, and catechol and resorcinol, with an oxidizing agent, likewise caused vulcanization. It should be mentioned that anthraquinone has not yet been made to work satisfactorily. All these reactive substances have two reactive groups in them, and this fact fitted in nicely with the bridge theory. Then came the surprises; simple primary and secondary aromatic amines also work in the presence of an oxidizing agent (some of them very

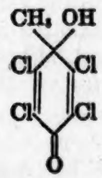
well) as well as simple phenols and thiophenols. Since the amines and phenols can form quinones by oxidation or can exist, at least theoretically, in the quinonoid form by tautomeric rearrangement,



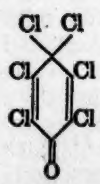
it may still be that these also fall in the same general class as the quinones and the quinonimines. Whether the rubber adds to the quinonoid structure or whether the active hydrogens of the quinonoid structure or of the hydroxyl or imino groups add to the double bonds in the rubber are questions which cannot yet be settled. Further work in an effort to help settle the matter showed that pentachlorophenol, tetrabromo-*o*-cresol, tetrachloro-*p*-cresol, mesitol, and even penta-methylphenol, with lead chromate as the oxidizing agent, give excellent vulcanizates. In these examples all the other hydrogens on the nucleus are replaced. The halogens could be considered as somwhat labile and therefore possibly reactive, but the methyl groups in pentamethylphenol are very stable. But this can also exist in the quinonoid form and could fit into one of the two general schemes.

The addition of amines[25], phenols[32] and thiophenols[44] to unsaturated hydrocarbons is known. Generally catalysts such as concentrated sulfuric acid and an amine hydrochloride are necessary, and sometimes temperatures above those ordinarily used for vulcanization are required. However, there is no theoretical reason why these substances should not add to rubber hydrocarbon.

A quinole, 2,3,5,6-tetrachloromethylquinole,



was prepared and tested, since it has the quinonoid structure and yet is not a quinone. It was tried alone in rubber, and with lead dioxide, zinc oxide and a mixture of red lead and magnesia, all of which work well with tetrachloroquinone; but the signs of vulcanization were meager. The lead dioxide mixture was "short" and might have been overcured. A similar compound with a quinonoid structure, hexachlorocyclohexadienone,



was also tested and gave a definite although weak vulcanizate. These results are not against and yet they are not strong for the quinonoid theory.

Perhaps a modification is necessary similar to that mentioned especially by van Rossem *et al.*[46] in his study of vulcanization with benzoyl peroxide—namely, that hydrogen atoms attached to carbon atoms adjacent to the position where

the reagent adds are oxidized off, and thus the two sections can form a bridge between two molecules or they can unite two parts of the same molecule.

To summarize, the quinonoid structure is an active grouping, is found in many of the vulcanizing agents, and therefore may play a part in the chemistry of vulcanization. However, a further study of all the reactions indicates that the hydroxyl, amino and imino groups may play an even more important part. The active grouping catalyzed perhaps by the oxidizing agent present seems to add to the rubber, and then this addition product seems to be oxidized to form the vulcanizate. Many reduced substances have been found and identified in vulcanizates prepared with tetramethylthiuram disulfide (tetramethylthiuram monosulfide), *m*-dinitrobenzene (probably dinitroazoxybenzene), benzoyl peroxide (benzoic acid), hexachlorodiazoaminobenzene (hexachlorodiphenylamine), quinone (hydroquinone), tetrachloroquinone (tetrachlorohydroquinone), *N*-phenylquinonimine (*N*-phenyl-*p*-aminophenol), quinone-*bis*-phenylimine (*N,N'*-diphenyl-*p*-phenylenediamine), etc.

It was found by experiment that tetrachlorohydroquinone does not readily add to the rubber hydrocarbon under the same conditions of vulcanization. From a mixture of rubber and tetrachlorohydroquinone after the usual heating in a press, all the tetrachlorohydroquinone could be extracted. This observation is not against the addition of this reagent since, as mentioned above, a catalyst is generally necessary for such a reaction.

If the mechanism of practically all, if not all, the nonsulfur agents involves an oxidation-reduction reaction, how does sulfur itself fit into this picture? The author postulates that if sulfur reacts as these other substances seem to do, since it exists in the oxidizing condition, it should first be reduced to hydrogen sulfide which, in turn, should add to the rubber, and then the rubber-hydrogen sulfide addition product should be oxidized by the remaining elemental sulfur to form the vulcanizate. This is logical, although it may seem somewhat revolutionary. Let us look briefly at sulfur vulcanization and then see how well this hydrogen sulfide theory fits the facts.

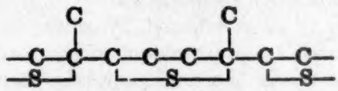
THEORIES OF SULFUR VULCANIZATION

This subject has been so well and completely treated by Kindscher[81], van Rossem[45] and Williams[54] that only a few outstanding facts and their significance will be presented.

Vulcanization is accompanied by the chemical combination of sulfur with rubber hydrocarbon. The reaction is considered to be irreversible, since every attempt to remove the sulfur has resulted in the disruption of the rubber molecule. The rate of addition is constant and independent of the proportion of sulfur present, even when the amount is small and all of it is in solution. It is a true chemical reaction, since the temperature coefficient lies within limits assumed for chemical reactions. It is believed that the sulfur in some way saturates double bonds, since the proportion of double bonds is diminished by an amount equal to that calculated on the basis of one double bond for each atomic equivalent of combined sulfur. The fact that hydrogenated rubber which is a saturated compound cannot be vulcanized[50] is evidence that the double bonds pay some part in the vulcanization reaction.

The type of chemical combination is not known, and practically none of the types proposed have experimental work to substantiate them. Since sulfur chloride reacts with simple olefins uniting two molecules with a sulfur bridge, it

has been postulated by many authors that sulfur forms bridges between molecules of rubber. The reaction of sulfur vulcanizates with methyl iodide indicates that part of the combined sulfur is in the form of thioether linkages, R—S—R[35], but serious doubt has recently been cast on this conclusion by Brown and Hauser[11], and Williams[56], and Smallwood[47] concludes that it is wholly unwarranted. A thiophene linkage has also been proposed:



from the types of thiophenes found by destructive distillation of ebonite[37].

Decrease in solubility is associated with increase in molecular weight in large molecules, and therefore polymerization has been considered as taking place in vulcanization. Sulfur and benzoyl peroxides are polymerizing agents, and both vulcanize rubber. Polymerization means loss of some unsaturation, and no loss other than that accounted for by combined sulfur can be detected, since it would be too small to be estimated by present chemical methods. Polymerization should mean a decrease in volume, but high pressures have been found to give no change in volume or in properties, even when the rubber is swollen with isoprene[54]. Under very high hydraulic pressure and high shearing stress, Bridgman[10] found that rubber is converted into a hard, translucent hornlike material. Isoprene alone under high pressures polymerizes to produce a vulcanized type of rubber.

It has been postulated that a small portion of the rubber becomes completely saturated with sulfur and that this polyprene sulfide is then dispersed in the raw rubber and thus forms the vulcanizate. Experiments to prove this have all failed.

Until recently all the evidence showed that the rubber-sulfur products were homogeneous, and every effort to fractionate vulcanized rubber failed to show any difference[2]. Using purified rubber partially vulcanized to a sulfur content of only 0.06 per cent, Midgley, Henne, Shepard, and Renoll[38] obtained three fractions by fractional precipitation; the second and third fractions had two and three times the sulfur content of the first. Williams[56] peptized several samples of well vulcanized rubber, with the usual proportion of combined sulfur, by means of piperidine in toluene and fractionally precipitated them with ethyl alcohol. These fractions had fairly wide variations in their sulfur content. He concluded that "no direct evidence exists to support the sulfide theory of vulcanization".

The formation of polar groups on the rubber molecule is said to be essential to produce vulcanization. Natural crude rubber is a nonpolar material, and vulcanization increases the polarity of the rubber[52]. Since vulcanization with Grignard reagents gives a complex which probably contains polar groups, this theory is given some support[36].

Boggs and Blake[9] assume that there are two types of unsaturation in rubber; that the saturation of one type (the end double bonds) gives soft rubber, and that of the other type (the remaining double bonds), hard rubber; and that both reactions go on at the same time. They base their theory chiefly on the amount of heat produced in the reactions.

From his study of methods to determine the extent of vulcanization, Garvey[22, 23] concluded that during vulcanization there are at least two reactions—a combination of the agent with rubber, and an unknown reaction of the rubber hydrocarbon catalyzed by the vulcanizing agent.

NEW HYDROGEN SULFIDE THEORY

Let us return now to the application of the generalization obtained from the study of the action of nonsulfur vulcanizing agents to sulfur vulcanization and the theory developed from it. The hydrogen sulfide theory proposes that:

Hydrogen sulfide, which is formed by the action of sulfur with the nonrubber components or rubber hydrocarbon itself, adds to a double bond in a molecule of rubber hydrocarbon, forming a mercaptan.

The rubber mercaptan is then oxidized by sulfur to form a disulfide, and hydrogen sulfide is generated as a by-product of the reaction. If the mercaptan groups which are oxidized are in the same molecule, then the disulfide structure will unite two portions of the same molecule, and if they are in different molecules, the disulfide structure will form a bridge connecting two molecules.

The hydrogen sulfide generated as a by-product may react with another double bond and thus continue the reaction.

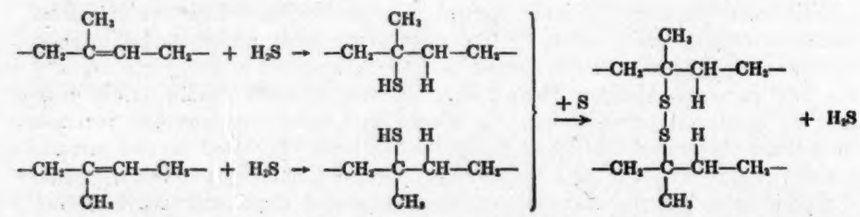
Sulfur may catalyze the addition of hydrogen sulfide to a double bond.

The reaction may be a chain reaction, and then there would be only a small amount of hydrogen sulfide left over at the end.

Organic accelerators may act in two ways: (*a*) to catalyze the addition of hydrogen sulfide to a double bond and possibly also to catalyze the oxidizing action of the sulfur, and (*b*) in many cases to give hydrogen sulfide by reaction with sulfur.

Inorganic accelerators may act as they are or, in the form of the corresponding sulfides, like organic accelerators, except that they cannot readily help to supply hydrogen sulfide.

An organic chemist's idea of such a reaction can be illustrated with two sections of rubber structure as follows:



ARGUMENTS FOR THE THEORY.—The theory postulates that there should be a loss of one double bond for each atomic equivalent of sulfur chemically combined. This is in accord with the facts.

The Peachey process of vulcanization with hydrogen sulfide and sulfur dioxide[43] is easily explained by the theory. The sulfur required for the oxidation could be supplied by the interaction of the two gases. Also, sulfur dioxide is an oxidizing agent and could oxidize the $-SH$ groups. This statement is given support by the work of Hock and Schmidt[26], who show that it is the rubber which causes reaction between the two gases and emphasize the fact that the vulcanizing reaction begins even with dry rubber. No reaction occurs in the absence of rubber between the two gases at room temperature when they are dry.

That hydrogen sulfide is present during vulcanization is shown by the odor of the gas during the heating of a rubber-sulfur mix, especially when the press is opened, and also by the fact that certain metallic oxides such as zinc oxide, ferric oxide, and litharge are converted into the corresponding sulfides. These oxides are not converted into the sulfides by elemental sulfur at the temperatures used.

If hydrogen sulfide adds to rubber in the preliminary stages of vulcanization, then vulcanization should proceed more rapidly and show a greater proportion of combined sulfur in an atmosphere of hydrogen sulfide than in air. Buizov and Popova[14] studied the "influence of the gaseous medium on hot vulcanization", and found that vulcanization does proceed more rapidly in hydrogen sulfide than in air, and still more rapidly when the hydrogen sulfide is mixed with steam. No analyses of combined sulfur were reported. Sulfur dioxide showed the least influence of all the gases studied; in fact, it showed a retarding influence. It is of interest that ammonia was close to hydrogen sulfide. The compound used consisted of rubber 93, sulfur 6.5 and magnesium carbonate 0.4, and was heated for 60 and 120 minutes at 135-138° C. Some of the results are given in the following table:

Gas	% free sulfur	
	60 min.	120 min.
Sulfur dioxide	5.63	5.06
Air	5.44	4.86
Vacuum	5.20	4.09
Ammonia	4.58	3.50
Ammonia and steam	4.54	2.86
Hydrogen sulfide	4.32	2.96
Hydrogen sulfide and steam	4.05	2.27

The method of sulfurizing olefin bonds with sulfur in the presence of hydrogen sulfide, including the vulcanization of rubber, was patented by Alexander and Posnansky[1]. Ammonia, amines, and accelerators are used as sulfur carriers.

Vulcanization of a rubber-sulfur mix *in vacuo* should not be so good as when it takes place at or above atmospheric pressure, on account of the loss of hydrogen sulfide. This was found to be the case by Zhavaronok[50], although his explanation is different.

The evidence for the addition of hydrogen sulfide to double bonds is very recent, little being available when the theory was first proposed. Usually and probably always catalysts are necessary, including sulfuric acid, ammonia and amines, peroxides, metal sulfides, and especially sulfur, and sometimes temperatures as high as 200-300° C.[3, 15, 16, 28, 30, 39]. Jones[29], working with E. E. Reid, gave some interesting results on the addition of hydrogen sulfide and mercaptans to propylene, and Böeseken and Linde[7] found that there is a reaction between hydrogen sulfide and isoprene only when a catalyst such as ferrous sulfide is present, and then both mono- and dihydrogen sulfide addition products are formed at temperatures up to 100° C. Meyer and Hohenemser[35] treated cyclohexene with sulfur at 150° C and obtained cyclohexyl mercaptan and dicyclohexyl sulfide, but no cyclohexenyl mercaptan and no cyclohexenyl sulfide. Their results can readily be explained by the formation at first of hydrogen sulfide and the addition of it to the double bonds.

The addition of mercaptans to double bonds was described in 1905 by Posner[44]. In this connection mention is made of the addition of thioglycolic acid, $HS.CH_2COOH$, to rubber[27]. The addition product is soluble in aqueous alkali, and therefore it would appear that the mercapto group adds to the double bond and the carboxyl group is free. Thioglycolic acid does not vulcanize rubber even in the presence of an oxidizing agent.

Arguments against the Theory.—The theory requires a disulfide structure, and there is no experimental proof for such a structure.

No addition product of rubber and hydrogen sulfide has been isolated. Efforts of the author to prepare a rubber mercaptan were fruitless.

If the hydrogen of the added hydrogen sulfide comes from rubber hydrocarbon, then the hydrogen content of the vulcanizate will be the same as when it is assumed that only elemental sulfur is added. If it comes entirely from non-rubber components, then the vulcanizate will contain extra hydrogens. The actual amount of this extra hydrogen will be small and not easily determined, but if enough hydrogen can be obtained from outside sources and enough sulfur is present to form hard rubber, then the differences can easily be determined. No determinations of carbon and hydrogen could be found in the literature; therefore Fisher and Schubert[20] performed some experiments, with the result that no extra hydrogen was found.

Assuming the minimum number of isopentene units in the rubber molecule to be 100, the formula of rubber hydrocarbon would be $C_{500}H_{800}$, and the formula for a vulcanized rubber containing about 4.5 per cent of combined sulfur would be $C_{500}H_{800}S_{10}$. The corresponding vulcanized molecule formed through the initial addition of hydrogen sulfide would be $C_{500}H_{810}S_{10}$. The composition of these last two would be as follows:

	$C_{500}H_{800}S_{10}$	$C_{500}H_{810}S_{10}$	Difference
C	84.186	84.068	−0.118
H	11.315	11.439	+0.124
S	4.499	4.493	−0.006
Total	100.000	100.000	

These figures show that it would be difficult to distinguish between two such compounds by analysis. However, if the same reaction continued until every double bond is saturated—in other words, until hard rubber is formed—then the formula for the final product would be $(C_5H_9S)_x$, or on the same molecular basis as above, $C_{500}H_{900}S_{100}$. The corresponding present-day accepted formula is $(C_5H_8S)_x$ or, again using the same molecular basis, $C_{500}H_{800}S_{100}$. The composition of these last two would be as follows:

	$C_{500}H_{800}S_{100}$	$C_{500}H_{900}S_{100}$	Difference
C	59.923	59.326	−0.597
H	8.054	8.970	+0.916
S	32.023	31.704	−0.319
Total	100.000	100.000	

REMARKS

In the formation of soft rubber, the rate of addition of sulfur is constant, regardless of the proportion of sulfur present. Perhaps the combination of the reactions outlined in the new theory will explain the formation of the straight-line curve obtained when the reaction rate is plotted.

Perhaps also the theory explains Garvey's second postulation in his attempt to outline the course of vulcanization—namely, that there is a reaction of the double bonds of the hydrocarbon which does not involve sulfur.

The vulcanization at room temperature of rubber mixtures containing sulfur, tetramethylthiuram disulfide and zinc oxide, which have been exposed to hydrogen sulfide, was explained by Bedford and Sebrell[4] by their polysulfide theory. It may be that the new theory will explain this reaction more satisfactorily.

Dibenzyl disulfide does not vulcanize rubber, either alone or in the presence of an oxidizing agent, whereas thiophenols, which are derivatives of hydrogen sulfide, do vulcanize rubber in the presence of oxidizing agents. This is especially interesting since thiophenols readily form disulfides outside of rubber in the presence of mild oxidizing agents.

Since hydrogen sulfide and water have some properties in common, can water be chemically combined with rubber hydrocarbon and the resulting product be oxidized to form a vulcanizate? In other words, can rubber be vulcanized with water and an oxidizing agent? Several experiments were tried but none was successful.

On the basis of the hydrogen sulfide theory the author predicted that phenols and thiophenols would vulcanize rubber in the presence of oxidizing agents, and experiments bore out this prediction.

In this world of today it is believed that work with the nonsulfur vulcanizing agents is laying the foundation which in the world of tomorrow will furnish the key to the solution of the baffling problem of the chemistry of rubber vulcanization.

RÉSUMÉ

The early history of vulcanization and the beneficial changes wrought on rubber by Goodyear's famous process are reviewed. An outline is given of the methods used in vulcanization, the principal facts and the theoretical considerations of the chemistry involved. Nonsulfur vulcanizing agents are listed, including some not previously described, yellow mercuric oxide and the combination of phenols and oxidizing agents. A comparison of their chemical activity brings forth the generalization that probably in all cases a reduction and an oxidation take place. If the agent is already in the reduced state, then it is necessary to add an oxidizing agent. An oxidizing agent generally makes a better vulcanizate with almost all nonsulfur agents. The reduced form probably adds to the rubber hydrocarbon, and this addition product is then oxidized to make the vulcanizate.

Since all vulcanizates have certain characteristics in common, it is postulated by analogy that some of the sulfur during vulcanization is reduced to hydrogen sulfide, that the hydrogen sulfide adds to rubber hydrocarbon, forming a mercaptan, and that this mercaptan is oxidized by some of the sulfur to form a disulfide which may connect two sections of the same or of two different molecules. It is shown that many of the facts of sulfur vulcanization are explained by this theory.

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CHEMICAL REACTIONS DURING VULCANIZATION *

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The data and material of a previous article[4] will be referred to directly, and the same nomenclature and terms will be used. The first article presented data on four accelerated stocks compounded according to the basic formula given in Figure 1, but employed a different accelerator in each stock. They were designated as stocks A (tetramethylthiuram disulfide), B (mercaptobenzothiazole), C (zinc dimethyldithiocarbamate), and D (heptaldehydeaniline). Stock E, a plain rubber-sulfur compound, containing 100 parts of rubber and 8 parts of sulfur, was also studied.

The experimental procedure for stocks G, H, and J (Figure 1) was identical to that previously described, except for the thiuram disulfide stock J, where the combined sulfur was determined directly on acetone-extracted samples. With this active vulcanizing agent it was found necessary to extract in the cold to prevent further cure. Accordingly for both the unsaturation and combined sulfur determinations, the samples were extracted in the cold with the apparatus described by Lindsly[13]. The experimental data are given in Table I, and the physical and chemical properties are plotted against the time of cure in Figure 1.

The combined sulfur and unsaturation curves for stock H show a noticeable break around 20 to 30 minutes, just as if a more active accelerating agent were being released at that time to speed up the reaction of sulfur and the loss of double bonds. The experimental values of these points were checked several times to make certain that the change in trend was definitely outside the experimental error of the measurements. The accelerator in stock H, "Ureka C," is the benzoate of mercaptobenzothiazole, in which the acidic hydrogen atom has been replaced by a benzoyl group. The action of heat is evidently causing the ester to break down and liberate the more active mercapto accelerator after 20 to 30 minutes. This chemical evidence agrees well with the general conception of the mode of action of such delayed-action accelerators. Figure 1 again shows, in supplementing stocks A to E previously studied, that the loss in unsaturation alone, like combined sulfur, does not explain the change in tensile strength of a vulcanized stock during cure. The same is true for the modulus.

CORRELATION OF LOSS IN UNSATURATION WITH PHYSICAL PROPERTIES

Since the changes in tensile strength with time of cure are generally considered to be a measure of the building up of a new (vulcanized) structure in early parts of the cure, as well as the ability to maintain that structure during overcure, the maximum tensile strength is usually considered indicative of the optimum physical state of the compound. Since this optimum state is also the one desired from a practical viewpoint, tensile strength is generally accepted as an important criterion of vulcanization.

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A comparison of the combined sulfur at the highest tensile strength for each stock reveals no significant correlation. However, a plot of the total change in unsaturation, $\triangle U_t$, against the highest tensile strength for each of the stocks

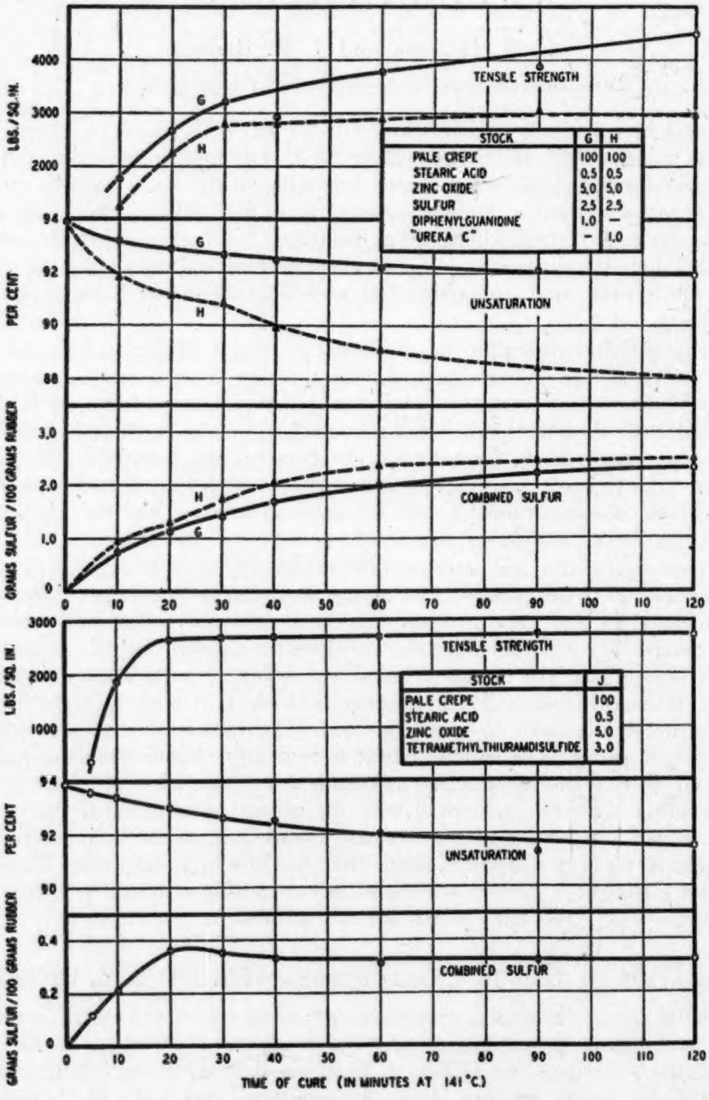

FIG. 1.—Physical and chemical properties of stocks G, H, and J *vs.* time of cure.

studied shows that the optimum tensiles for stocks containing both sulfur and accelerator are better with low $\triangle U_t$ (Figure 2). In other words, at the optimum point of each cure (highest tensile) the accelerated stock which has lost the least number of double bonds will have the highest tensile strength. For two of

the accelerators studied, the loss of only 2 per cent of the double bonds existing before cure is necessary to achieve optimum tensile strength.

TABLE I

SUMMARY OF DATA ON STOCKS G, H, AND J

Stock	Time of cure at 141° C (286° F) (min.)	Combined S per 100 grams of rubber (grams)	Unsaturation (%)	Tensile strength (lb. per sq. in.)	Modulus at 500% (lb. per sq. in.)	Elongation at break (%)
G	0	0.00	93.9	—	—	—
	10	0.74	93.2	1760	130	1065
	20	1.13	92.9	2685	175	935
	30	1.40	92.7	3210	275	875
	40	1.70	92.5	2940	305	815
	60	2.01	92.2	3780	405	815
	90	2.22	92.1	3880	430	815
	120	2.31	91.9	4500	505	805
	8 hr.	2.47	91.2	1950	175	900
H	0	0.00	93.9	—	—	—
	10	0.95	91.8	1240	105	1005
	20	1.29	91.1	2250	160	1020
	30	1.72	90.8	2800	200	910
	40	2.04	89.9	2800	240	885
	60	2.36	89.1	2900	260	905
	90	2.45	88.4	3070	260	905
	120	2.49	88.0	2980	250	910
	8 hr.	2.49	87.6	2210	180	905
	0	0.00	93.9	—	—	—
	5	0.12	93.6	390	105	965
	10	0.21	93.4	1875	160	940
	20	0.36	93.0	2650	250	850
	30	0.35	92.6	2700	300	815
	40	0.33	92.5	2710	305	810
	60	0.31	92.0	2710	345	790
	90	0.32	91.3	2760	340	790
	120	0.32	91.5	2720	335	785

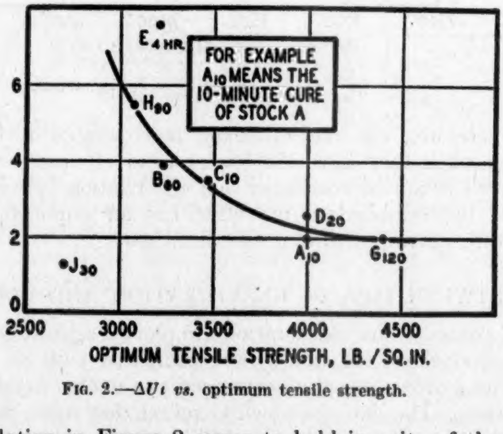

FIG. 2.—ΔU_t *vs.* optimum tensile strength.

This general relation in Figure 2 seems to hold in spite of the wide range of time of cure necessary to reach optimum tensile strength. The time for maximum cure of the different stocks is indicated by the subscripts to the letters on the

curve. Stock E (100 rubber—8 sulfur) and stock J (containing tetramethylthiuram disulfide as a curing agent without added sulfur) do not fall on the curve, but it must be remembered that their combined sulfur contents are quite different from those of other stocks. However, when equivalent atoms of combined sulfur are used as a basis, the loss in unsaturation of these two stocks can be correlated with the others. Thus,

$$\frac{\text{double bonds lost}}{\text{atom of combined sulfur}} = \left(\frac{\triangle U_t}{68}\right)\left(\frac{32}{S_c}\right) = \frac{\triangle U_t}{2.125\, S_c}$$

where U = unsaturation at given time of cure, %
$\triangle U_t$ = total loss in % unsaturation $= U_{\text{uncured}} - U$
S_c = grams combined sulfur per 100 grams rubber
68 = mol. weight of rubber hydrocarbon unit C_5H_8
32 = atomic weight of sulfur

A plot of the ratio $\triangle U_t/2.125S_c$ against the corresponding optimum tensile shown in Figure 3 reveals that all the vulcanized stocks can be correlated by the

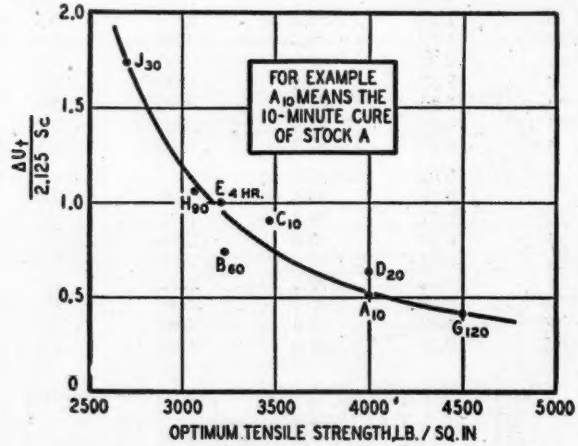

FIG. 3.—$\Delta U_t/2.125S_c$ *vs.* optimum tensile strength.

same curve. Therefore, both accelerated and unaccelerated stocks have the highest tensile strength when they have the lowest ratio of unsaturation to combined sulfur. From this it can be concluded that the relation between the loss in unsaturation and the combination of sulfur has an important bearing on the physical structure developed during vulcanization.

RELATION BETWEEN LOSS IN UNSATURATION AND COMBINED SULFUR

In Figure 4, values of the unsaturation are plotted against the amount of combined sulfur for stocks G, H, and J, and compared with the theoretical linear relations of 1 or 2 atoms of sulfur combined per double bond lost, as the solid straight lines show. The data for stock G reveal that sulfur is combining in the ratio of over 2 atoms of sulfur per double bond lost, whereas H and J show a ratio nearer 1. This variation is even greater than that previously observed for stocks A and E[4].

Stock H, containing the delayed-action accelerator, reveals a definite change in the type of sulfur combination between 20 and 30 minutes of cure, where the ratio changes from 1 to about 1.2. Thus, the action is not merely an increase in the rate of sulfur addition, since the active accelerating agent is released under heat, but must be considered as an actual change in the type of reaction involving sulfur and the double bonds.

Figure 4 shows that an increased loss of double bonds occurs after most of the sulfur has combined, and that this loss depends on the type of accelerator employed. This also was true of the first stocks studied. At that time it was uncertain as to whether the values for unsaturation represented the true state of the overcured compounds, or whether a loss of double bonds had occurred during the measurement of unsaturation.

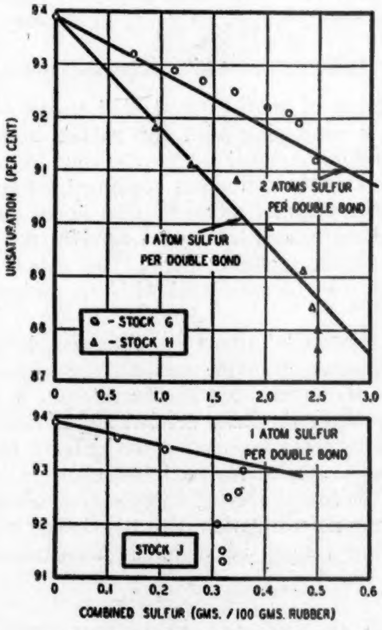

FIG. 4.—*U vs. S_c* for stocks G, H and J.

A study of the method of dispersing the vulcanized samples in *p*-dichlorobenzene revealed that the unsaturation values were not greatly affected by the time of heating or by the atmosphere of the operation, whether air or nitrogen. In the latter case, although the time for completely dispersing the overcured samples was increased about threefold in the absence of oxygen, the unsaturation values changed only to a small degree. The results for two of the overcured samples are shown in Table II. The precision of measurement with these overcured samples was not so good as with the shorter cures whose unsaturation values usually checked to within ± 0.1 per cent.

It is quite possible that not all traces of oxygen were excluded from the nitrogen. If such is the case, then small amounts of oxygen would be effective, and perhaps even necessary, in dispersing the vulcanized samples in heated solvents. Staudinger[20] reported that oxygen will degrade insoluble rubber and

cause it to dissolve; in an analogous case traces of oxygen were shown to be necessary in milling to reduce the rubber to the plastic state[5, 6]. Since breakdown of rubber on the mill causes no change in measurable unsaturation, the assumption seems permissible that traces of oxygen also cause the dispersion of vulcanized rubber without a measurable loss in unsaturation.

Table II

Effect of Oxygen on Measurement of Unsaturation

Stock	Cure (min.)	Atmosphere	Time of heating (min.)	Unsaturation (%)
H	120	Air	32	88.4
		N_2	115	88.8
J	90	Air	85	90.6
		N_2	200	90.8

CORRELATION OF LOSS IN UNSATURATION AND COMBINED SULFUR

A general consideration of all the accelerated stocks studied reveals that, in vulcanization, sulfur is combining with the rubber in a definite ratio of the number of atoms of sulfur combined per double bond lost, during the early parts of the cure. After most of the sulfur has combined, an additional loss of double bonds takes place due to polymerization by heat under the influence of accelerators or some similar effect caused by oxygen. These two reactions involving the unsaturation of the rubber molecule depend on the type of accelerator employed and, in general, may be correlated with the optimum physical properties of the vulcanizates.

Accelerators showing ratios of atoms of sulfur combined per double bond lost of 2 or more, produce higher optimum tensile strengths than accelerators showing ratios nearer 1. Also, the excess loss of unsaturation in the latter part of the cure is greater in most cases for those accelerators having a low ratio. The particular type of sulfur combination characterized by a high accelerator ratio is evidently contributing to the vulcanized structure to produce higher tensile strengths. However, the excess loss of unsaturation occurring with accelerators having a low ratio shows no correlation with the change in tensile strength during overcure, and therefore cannot be definitely associated with changes in the vulcanized structure.

CAUSE OF EXCESS LOSS IN UNSATURATION

In the case of accelerated stocks there is no direct evidence as to whether the increased loss of double bonds occurring after most of the sulfur has combined is due to polymerization by heat under the influence of accelerators or degradation of the molecule by oxygen. In the case of the simple rubber-sulfur compound stock E (100 rubber—8 sulfur) infrared absorption spectra on a thin film show no particular change after 3-hour heating of 140° C (284° F). After 10 hours, however, the presence of oxygen is definitely established in the form of C=O, hydroxyl and ether linkages, as well as a degradation in the hydrocarbon structure. This seems to be in good agreement with the infrared work of Stair and Coblentz[19] on the aging of natural rubber, and with the large excess loss in unsaturation observed for the 10-hour cure of stock E, which was accompanied by a decided loss of tensile strength from the optimum value of the 4-hour cure. Likewise, van Rossem and Dekker[18] recently showed that oxidation products may be developed during vulcanization as well as during aging.

TYPE OF SULFUR COMBINATION

It was previously pointed out that combination of sulfur in excess of 1 atom of sulfur per double bond lost could be explained as the result of several simultaneous reactions of sulfur with the rubber molecule. Possibilities of such combinations were suggested, such as sulfides, disulfides, thioozonides, mercaptans, and thiophene derivatives[4].

Chemical tests for all such compounds were applied to the stocks tested. The vulcanized samples were dispersed in *p*-dichlorobenzene as in the measurement of unsaturation and diluted with carbon tetrachloride to assure a liquid solution. The use of nitrous acid indicated the absence of mercaptans[16] and thiophenes[12]. Sodium arsenite and potassium cyanide gave no indication of disulfides[11]. Isatin in sulfuric acid showed no evidence of mercaptans[8] or thiophenes[1]. Sodium nitroprusside gave no evidence of mercaptans[1] and, when modified as in Grote's reagent, was entirely negative in revealing the presence of $-SH$, $=C=S$, or

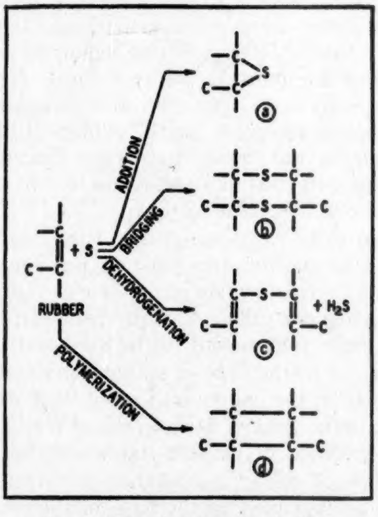

FIG. 5.—Reactions in vulcanization.

$-S-S-$ compounds[10]. Finally, attempts to detect mercaptans with sodium plumbite[9] were entirely negative. Although the applications of these chemical tests were not altogether satisfactory in some cases, owing to precipitation of the rubber from solution, it is felt that there is at least not much probability of these forms of sulfur combination being present in vulcanized rubber to any great extent.

The combination of sulfur with substances other than rubber hydrocarbon was previously shown to be small enough to be neglected. Further tests for zinc sulfide in the compounded stocks by the method of Stevens[21] showed it to be less than 0.1 per cent of sulfur on the rubber, which agrees well with the work of Brazier and Ridgway[3].

Although previous work has shown the methyl iodide reaction of Meyer and Hohenemser[14] to be invalid in a quantitative sense, it does indicate that sulfur has combined with the hydrocarbon, either by addition or as a bridge between adjacent double bonds (Figure 5, *a* and *b*). Both of these types would

produce a ratio of 1 atom of sulfur per double bond lost, as was found in the plain rubber-sulfur compound. If this ratio is to be greater than 1, an additional reaction must be taking place where sulfur can combine without loss of unsaturation. Such a possibility would be, for instance, a dehydrogenation reaction (Figure 5, *c*).

Although hydrogen sulfide is known to be given off during vulcanization[17] of pure rubber-sulfur compounds, no such data exist for accelerated stocks. In the present case it is not likely that much hydrogen sulfide was lost during the cure since the total sulfur remained practically constant in all stocks. If any dehydrogenation did occur, the hydrogen sulfide must have remained in the sample for the most part. It is possible that it could be oxidized back to free sulfur available for further vulcanization, but such a reaction would require enough oxygen to remove all the displaced hydrogen as water. If 1 gram of sulfur per 100 grams of rubber were combined in a dehydrogenation reaction, the oxygen required to combine with the displaced hydrogen would be only 0.5 gram. Although this is more than the free oxygen dissolved in pure gum rubber (according to Williams and Neal[7] dissolved oxygen is about 0.02 per cent for normal conditions), oxygen may have entered in during milling to form peroxides or other agents which might attack the hydrogen sulfide formed. (Cramer[7] recently found an increase in oxygen content of 0.12 per cent after 30-minute milling.) A further possibility is the absorption of oxygen by the rubber buring cure in the molds. It is well known that stocks will blister due to gas formation when not enough pressure is applied during cure, but in a press cure it is hard to predict just what happens to possible gaseous by-products.

Reactions of hydrogen sulfide with unsaturated hydrocarbons do not seem to have been studied much in the literature, so that possible reactions of this type cannot be predicted. Another possibility in the case of thiuram disulfide accelerators is the reaction of hydrogen sulfide to form dithiocarbamic acid (a good accelerator) and free sulfur, as pointed out by Bedford and Gray[2].

Experimental evidence as to the type of sulfur combination in vulcanization is noticeably lacking. However, the existence of more than one type of combination finds additional support in the work of Midgley[15] and Williams[22], who fractionated vulcanized rubber into portions of varying sulfur content.

The fact that the type of sulfur combination is evidently controlled by the accelerator present can be explained on the basis of the relative catalytic control over one or more of the reactions taking place. For example, accelerators having a high ratio of atoms of sulfur combined per double bond lost might favor the dehydrogenation reaction in preference to simple addition or bridging.

CONCLUSIONS

Direct addition or bridging of sulfur seems to occur at the double bonds of the rubber in sulfur vulcanization without accelerators (Figure 5, *a* and *b*). In accelerated stocks the fact that sulfur combines in excess of one atom of sulfur saturating one double bond of the rubber hydrocarbon suggests that sulfur may also combine in a dehydrogenation reaction (Figure 5, *c*), and that this type of sulfur linkage is most effective in producing high tensile strengths. The excess loss in unsaturation on overcure indicates that direct polymerization without sulfur (Figure 5, *d*), as well as reactions of oxygen at the double bonds, may occur after most of the sulfur has combined, but that these chemical changes are not definitely associated with changes in the vulcanized structure as measured by tensile strength. In the vulcanization of a simple rubber-sulfur compound,

infrared absorption data indicate that oxygen is combining with the rubber during overcure to produce a degradation in the hydrocarbon structure which is accompanied by a decided loss in tensile strength.

ACKNOWLEDGMENT

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COMPOSITE NATURE OF THE STRESS-STRAIN CURVE OF RUBBER *

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Stress-strain curves have been of great value in developing rubber compounds to their present state of usefulness. Special data such as the load at a given elongation or the elongation at a given load have been plotted against time of cure to determine the rate of cure or reversion characteristics. The quality of crude rubber has been judged by the tensile strength of its vulcanizate or by the slope of the stress-strain curve[8]. Tensile strength or stress-strain data are commonly used to follow the deterioration of rubber under either natural or artificial aging. The shape of the stress-strain curve has served as the basis for speculations regarding the structure of rubber, and attempts have been made to produce an equation from theoretical considerations which would reproduce the curve[6].

The stress-strain curve is known to be indefinite[1, 2, 7, 10] and a composite structure for the stress-strain curve has been indicated[4, 9]. Successive elongation cycles produce curves which reveal a lower load-carrying capacity at a given elongation. A condition approaching equilibrium is reached only after a considerable number of elongation and retraction cycles. In spite of all that is known in regard to the stress-strain cycle, most data are obtained from rubber which is strained to the breaking elongation on the first extension, and no attempt is made to study the retraction. In many cases only the tensile strength is considered, in spite of the fact that most rubber is strained in service only to a low elongation.

The effect of temperature on the shape and position of the stress-strain curve requires further study. Certain data[5] indicate that many compounded stocks become less resistant to deformation as the temperature is increased. Other data[1, 10] show that rubber which has been stretched repeatedly will be more resistant to deformation at elevated temperatures. The conflicting nature of these and other data made it appear desirable to investigate more carefully the lower elongations of the stress-strain curve.

APPARATUS

An apparatus has been designed which is sufficiently sensitive to record the stress-strain relationship during the first stages of the elongation and which can be operated over a wide temperature range. The test-pieces consist of rings, 11.318 mm. inside diameter, 14.146 mm. outside diameter, and 1.414 mm. thick, which are formed by molding. The small cross-section of the rubber permits it to assume the temperature of the bath quickly and permits the test to be conducted under approximately isothermal conditions. The load is applied by means of the apparatus shown in Figure 1.

L is a balanced assembly, including a variable-speed motor, *M*, which moves weight *W* along the beam by means of screw *S*. The assembly is sensitive to a load of 5 grams applied at the end of the lever. The load imposed by moving the weight is transmitted to the sample by means of a fine steel wire which passes

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from the end of the beam over the grooved pulley, *P*, and connects with the sample contained in the glycerol or water bath, *B*. Drum *D* is attached to the pulley and serves to hold the chart upon which the data are recorded. Elongation of the rubber causes a corresponding rotation of the drum. A nonelastic thread, *T*, is attached to the weight and passes over a pulley at the fulcrum and over the guide pulleys required to produce a lengthwise motion of the recording pen along the drum. The motion of the pen in this direction records the load, and the reducing pulley, *R*, is proportioned so that 1 mm. on the chart equals 1 kg. per sq. cm. of the test sample. The diameters of pulley *P* and drum *D* are such that 1 mm. on the chart equals an elongation of 10 per cent. The data are recorded on ordinary millimeter cross-section paper. The data in this paper were obtained by operating the machine at such a speed that a load of 60 kg. per sq. cm. could be applied and removed in 1 minute.

The machine operates with sufficient accuracy so that duplicate test-specimens can be expected to produce curves which will be exactly superimposed. If the stretching is repeated, the corresponding later cycles will also be superimposed. Figure 2 shows the end and side views of the instrument.

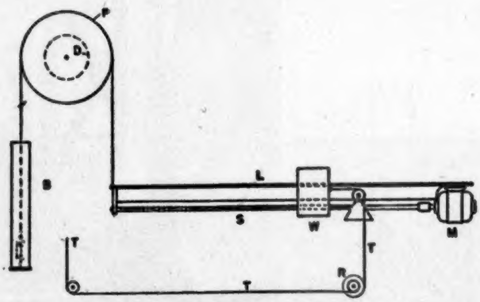

FIG. 1.—Diagram of testing machine.

The character of the stress-strain curve is revealed only after the rubber has been stretched to a considerable elongation several times. This causes a progressive change in the shape and position of the curve which is well established after the rubber has been strained four or five times to a high elongation.

CHARACTER OF STRESS-STRAIN CURVE

The stress-strain curve in its final shape may be divided into three well-defined sections. The first section extends to an elongation which may vary from 350 to 450 per cent at ordinary temperature. This section approaches a straight line but is slightly S-shaped, the first portion being concave to the elongation axis while the last portion is slightly concave toward the load axis. The modulus of elasticity is relatively low. The second section extends over about the next 100 per cent elongation. This section tends to become parallel with the elongation axis. The third section changes direction almost abruptly, and the rubber assumes a high modulus of elasticity. This section also approaches a straight line but is somewhat concave toward the load axis.

The changes described are illustrated in Figure 3. The curves were obtained with rubber containing 3 per cent of sulfur, 5 per cent of zinc oxide and 1 per cent Acrin accelerator (benzyl chloride addition product of hexamethylene-tetramine reacted with the sodium salt of 2-mercaptobenzothiazole). The compound was vulcanized for 20 minutes at 130° C.

The second section of the curve is of the greatest significance in determining the character of the rubber. Any point on the curve below the second section represents a definite equilibrium between the load and the resulting strain[3, 9]. Once the transition point which marks the beginning of the second section is reached, the rubber will continue to elongate rapidly under a constant load. The rate of elongation, which is rapid at first, will decrease as the amount of elongation approaches a more or less well defined limit of 50 to 150 per cent. Once the

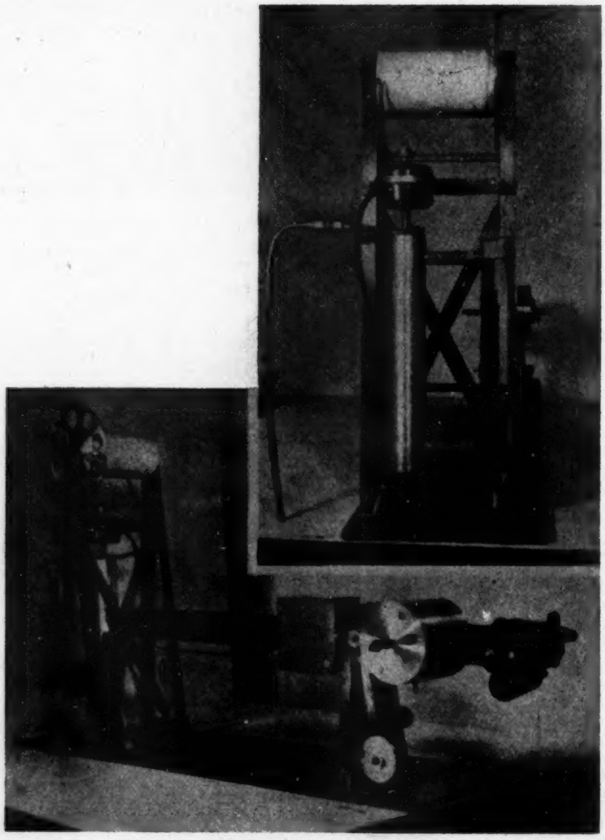

FIG. 2.—Views of testing machine.

flow is completed, the character of the rubber is altered and the remaining elongation may be carried out in apparent equilibrium with the load imposed.

The tendency for the rubber to flow under constant load is illustrated by Figure 4, which shows the fourth and fifth cycles obtained with the same rubber compound used in Figure 3. During the plotting of the fifth curve the machine was stopped for 3 minutes at elongations of 210, 350 and 620 per cent, and the rubber was permitted to remain under a constant load. Rapid flow occurred only at the transition point of approximately 350 per cent elongation. The load imposed at a lower elongation was not sufficient to produce a change in the rubber while the rubber again appeared to be relatively stable at higher elongations.

A permanent shift in the position of the curve is produced only after the rubber is strained to the transition point. While not strictly correct, this statement is essentially true and includes the first extension of the rubber. Figure 5 shows the result of five complete extension and contraction cycles, including the first, to an elongation below the transition point. The curves have not shifted sufficiently to produce distinct lines. Straining to a higher elongation will produce results similar to those shown in Figure 3.

The change in shape of the stress-strain curve persists for an extended time. The greatest effect, however, is evident if the series of curves are obtained over a short time interval, since there is some tendency for the rubber to revert to its original character after a prolonged rest period. A rest of several weeks may restore the rubber sufficiently so that the tendency to flow will be much decreased on the first cycle but will be fully developed on the second cycle.

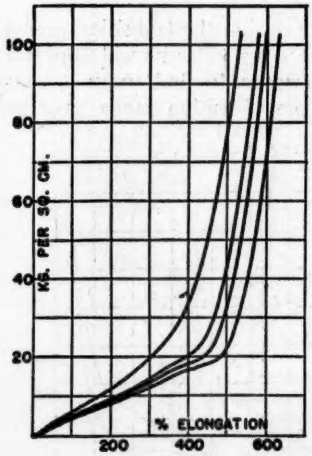

FIG. 3.—Shape of stress-strain curves illustrated by the first four elongation cycles.

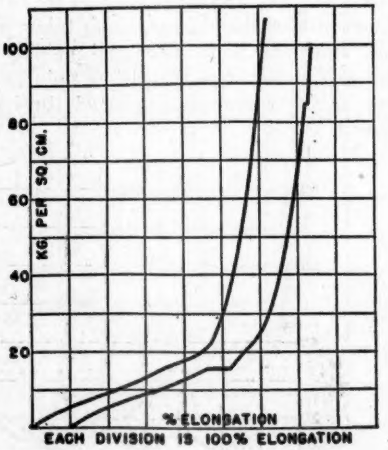

FIG. 4.—Flow of rubber under constant load.

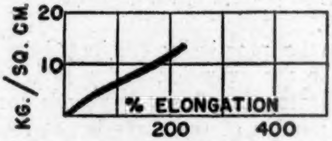

FIG. 5.—Reversible cycles at low elongation.

The principal hysteresis effects result from straining rubber to the transition point and appear to be connected with the flow which takes place in the second portion of the curve. When the transition point is exceeded, a hysteresis loop will be produced, the size of the loop depending on the amount by which the transition point was exceeded. Figure 6 represents the fifth to the ninth cycles, inclusive, and shows that the transition point can be approached closely before flow under constant load begins. The end of the flow period is not so evident. If all possible flow should take place at the transition point, the upper portion of the extension and retraction curves would be expected to coincide. Since this

does not happen, it is probable that flow continues under the increasing load but at a greatly diminished rate. This is indicated by Figure 4, which shows a small amount of flow at high elongation.

Figure 6 also shows that the retraction curve meets the extension curve at approximately the same position, regardless of the size of the hysteresis loop. It is also evident that contraction of the rubber has some tendency to take place under constant load. The flow takes place only when the load is considerably less than the load at the transition point on the extension curve. This indicates that a definite force must be imposed by the rubber before the reversal of the flow can be accomplished. The reversal is essentially complete, however, because the curve returns approximately to its origin.

The nature of the change which takes place during the transition period is not known. Both the Joule effect and possibly the x-ray patterns will appear at elongation well below the transition point. Attempts to find unusual changes in density as the rubber is elongated through the transition range have not been successful.

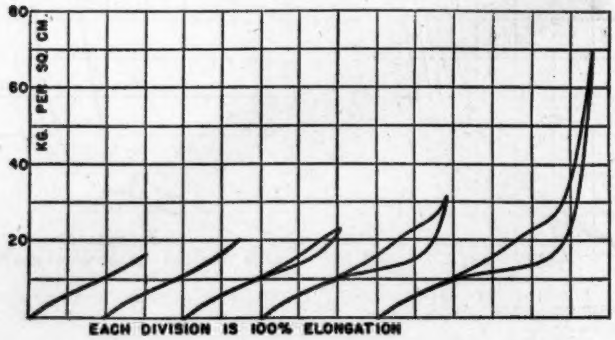

FIG. 6.—Hysteresis produced by straining beyond the transition point.

Hysteresis effects can be practically eliminated in the third section of the curve. Inability to make the extension and contraction curves coincide above the transition range indicates that flow takes place during the remainder of the stretching, so that this portion of the curve is not reversible under the present conditions of testing. The most probable location for reversible stretching at high elongation would be on the retraction curve between the point of maximum strain and the reverse transition point. This portion of the retraction curve is practically reversible, and rubber will contract and elongate within the specified limits without producing a hysteresis loop. If the contraction passes beyond the reverse transition point, a hysteresis loop will be formed. This phenomenon is illustrated in Figure 7, which shows three reversals on the contraction curve between elongations of 510 and 590 per cent, after which the elongation was reduced to 380 per cent. Elongation of the rubber from this position produced a new curve.

It is evident that rubber can be made to function in an efficient manner under two different conditions. Under the first condition the rubber follows the extension curve to some elongation below the transition point. The modulus of elasticity during this period is relatively low. Under the second condition the rubber follows the retraction curve below some point of maximum strain but above the reverse transition point. The modulus of elasticity under these conditions is

relatively great. The portions of the stress-strain curve which are reversible are indicated by solid lines in Figure 8.

The transition point of rubber is not greatly affected by the state of vulcanization when a given compound is considered. Increased cure will produce an initially higher modulus, but the transition elongation tends to remain almost constant. The greatest effect of increasing cure seems to be a slight decrease in the length of the second portion of the curve. The type of cure produced by different accelerators has more effect on both the position of the transition point and the extent of the transition range than variation of cure.

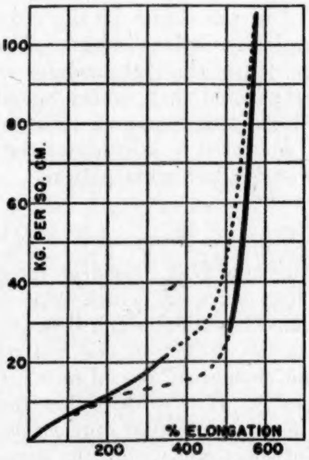

FIG. 7.—Reversibility of the retraction curve.

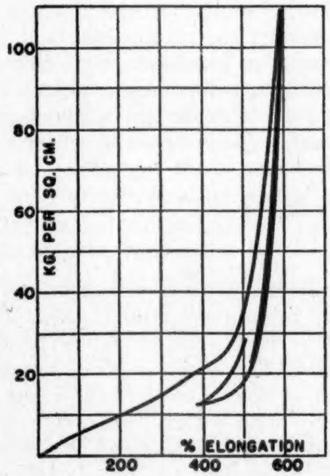

FIG. 8.—Reversible portions of the stress-strain curve.

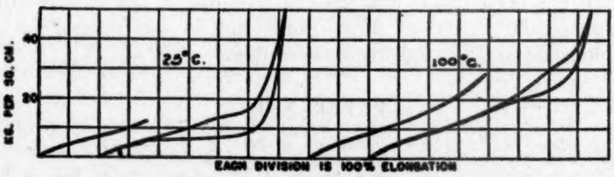

FIG. 9.—Effect of temperature on the position of the transition point.

The greatest change in the position of the transition point is caused by changes in the temperature. Rubber offers increasing resistance to flow as the temperature is increased. The transition point at 100° C will usually be found well above 600 per cent elongation. This means that rubber will function at 100° C with only slight hysteresis loss up to 600 per cent elongation. The hysteresis loop produced by stretching to a fixed elongation above the transition point is also greatly decreased at elevated temperatures. These effects are given by Figure 9, where complete cycles both below and byond the transition point are shown at 25° and 100° C.

The data presented in this paper were obtained with a compound which would withstand all the conditions imposed. Various accelerators produce rubber compounds with either greater or less flow during the transition period. Some of

these compounds will not withstand repeated stretching; while others become extremely brittle at elevated temperature. The changes which have been illustrated can, however, be detected with any pure gum type of rubber which has been tested. The effects are considerably masked by compounding ingredients and may not be observed with highly loaded stocks. This is due, at least in part, to the non-uniformity of elongation of the various fibrils of rubber in different positions between the particles of compounding ingredient. The resultant curve is a composite of innumerable overlapping curves which makes the transition from one position of the cure to the next less distinct. This does not mean that the effect is destroyed, but it is less intense at any position and extends over a greater portion of the stress-strain curve.

An interesting speculation exists in regard to the course of the stress-strain curve during very rapid extension. Since flow involves the element of time, it can be reduced by a reduction in the time cycle. Since the high-modulus rubber is produced only after the rubber flows, it is possible that rubber would follow an extension of the low-modulus curve to a high elongation at a sufficiently high rate of stretching. Such a possibility is also indicated by a study of the time of stretching in relation to the intensity of the x-ray diffraction pattern[3].

CONCLUSIONS

The stress-strain curve of rubber can be imagined to consist of three curves which tend to approach straight lines. The first curve has a high elongation load ratio and intercepts the second portion at an elongation which depends on the temperature. The second curve is parallel to the elongation axis and represents a condition of flow. The third curve has a low elongation to load ratio and represents rubber with a high load carrying capacity. It is evident that the second curve must be avoided as much as possible in most industrial applications. Most industrial applications require the rubber to work only within the limits of the first curve. The first curve is lengthened when the temperature is increased and the rubber can work efficiently to a higher elongation.

No evidence has been found regarding the nature of the change which occurs in rubber during the period of flow. Since the flow is reversible, it must be within the molecule and not between molecules.

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THE RESISTANCE OF RUBBER TO DYNAMIC FORCES

PART I *

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INTRODUCTION

The subject of the present paper, which is of great interest on account of the numerous service conditions under which rubber is subjected to dynamic forces, has received little attention, perhaps because of the complexity of the phenomena and the consequent difficulty of coming to any definite and significant conclusions from experimental data.

It is a widespread belief, for instance, that in static tension plastic flow takes place and that this is responsible for the Joule effect and that it modifies the shape of the stress-strain curve. By working at high velocities of extension, Williams[1] proved that at room temperature and also at 60° C the stress-strain curves are straight lines and that complete elastic recovery takes place. The importance of verifying such a conclusion as this is obvious. Since, in fact, the elongations for a given load found by Williams were in every case greater when the stress was static, one is led to the conclusion that the deformation brought about by a given load is the sum of two components; one a perfectly elastic component, which obeys Hooke's law and which therefore is applicable to the established science of construction; a second component, which, in contrast to the first, is plastic in character and consequently depends on the duration of application of the load and on the loads previously applied.

In brief, the law of deformation should be capable of reduction to the laws of two types of systems, *viz.*, an elastic system and a plastic system. Unfortunately however this assumption could not be confirmed.

The National Bureau of Standards[2] used only two tensile parameters, *viz.*, stress and strain and, as a result of tests at velocities of extension from 5 to 45 inches per minute, concluded that the greater the velocity of extension the greater are these two parameters.

Passing now to another aspect of the problem, van Rossem and Beverdam[3] made comparisons between the work of deformation necessary to cause rupture under tension by the ordinary Schopper dynamometer method and that necessary when rupture was caused by impact. They found in general that the work of rupture by slow application of a stress was much greater, *e. g.*, up to 5 or 5 times as great, as that by an impact force. The maximum value of the work of rupture by impact corresponded to a lower state of vulcanization than that obtained by the slow application of a stress. Also differences in the state of vulcanization could be detected more readily by the dynamic method than by the static method, but this was true only of rubber-sulfur mixtures with or without barytes or carbon black as necessary ingredients. In the case of mixtures containing zinc oxide, the trends of the two curves representing the energy of rupture as a function of the time of vulcanization at a given temperature

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become similar and the difference between the two values of the energy of rupture may even change sign.

Unfortunately these results seem to be at variance with certain otherwise alluring hypotheses which can be formulated, on a purely logical basis, from the experimental results of Williams, because the disappearance or reduction of the energy of plastic deformation associated with impact forces must be characterized by a constant decrease in the work of rupture with increase in the velocity of deformation. Without offering any further evidence, this observation itself is evidence that it is well to be cautious about drawing conclusions, for the phenomenon in question is by no means simple.

INITIAL WORK IN CARRYING OUT IMPACT TESTS

One of the great difficulties in impact tests like those of van Rossem and Beverdam (*loc. cit.*) arises from the changes in velocity while the test-specimen is being elongated. Whether resort is had to a pendulum, *e. g.*, the ordinary Charpy type for testing the resilience of metals, as was done by van Rossem and Beverdam, or whether, to assure simple linear extension, resort is had to a weight falling from a given height on the lower jaw (the upper jaw being fixed), as was done in the experiments to be described, the test-specimen undergoes considerable elongation, thereby dampens the motion and consequently diminishes the velocity of the object which collides with the test-specimen.

It is possible to utilize a high energy of impact so that the work of rupture of the test-specimen is negligible compared to it. In this case, the velocity of extension remains approximately constant, but the work of rupture still must be measured, and with considerable tolerance, because small errors in measuring the residual energy have a relatively great effect in estimating the work of rupture.

On the other hand, when a weight is allowed to fall from different heights or different weights from the same height, it is then possible to measure the work of rupture with a certain degree of precision, although account must be taken of the fact that in this case the velocity of extension is a variable, *i. e.*, it decreases with increase in the elongation. When this method is used, it is also possible to stretch the test-specimen below its point of rupture and thus to measure relative elongations under various conditions of stress.

This second procedure was adopted in the tests carried out in the present work. The experiments were made in 1934 in the Technological Laboratory of the Società Italiana Pirelli, which was at that time under the supervision of the present author.

A small, open, metal container, in which weights could be placed, was allowed to fall from the desired heights onto a plate, P, suspended from the lower grip, M_1, of two grips which carried the test-specimen. The upper grip, M_2, was suspended from the frame of the machine at F. The metal basket was guided in its motion by means of twelve wheels (twelve small ball-bearings) which ran along the guide rods, GG.

When the test-specimen ruptured or reached a predetermined elongation, the basket fell on a spring, m, and thus compressed it. By having first tared this spring it was possible to calculate the residual energy.

Since taring of the spring might be important enough to be taken into account, this also was carried out by the impact method, as is illustrated schematically in Figure 2, *i. e.*, the metal container, carrying weights totalling 10 kilograms, was made to fall from various heights directly on the spring and the compressions of the spring were read on a dial. The angle of rotation, α, of the pointer, I, was

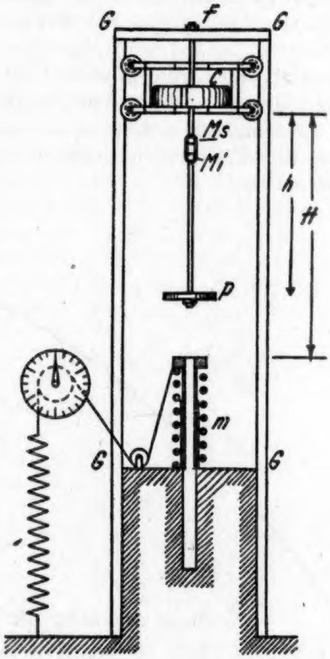

FIG. 1.

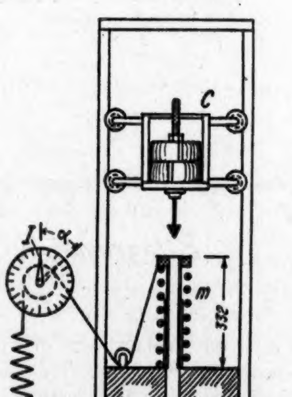

FIG. 2.

a measure of the potential energy of the falling mass, calculated by multiplying the weight of this mass by the total height of fall (total including the compression of the spring).

Figure 3 shows a curve of the tare measurements, with an indication of the degree of approximation obtainable in the interval which was used most frequently in the tests. By first making a test under static conditions, it was possible to establish the relation between the angle of rotation of the pointer and the compression of the spring.

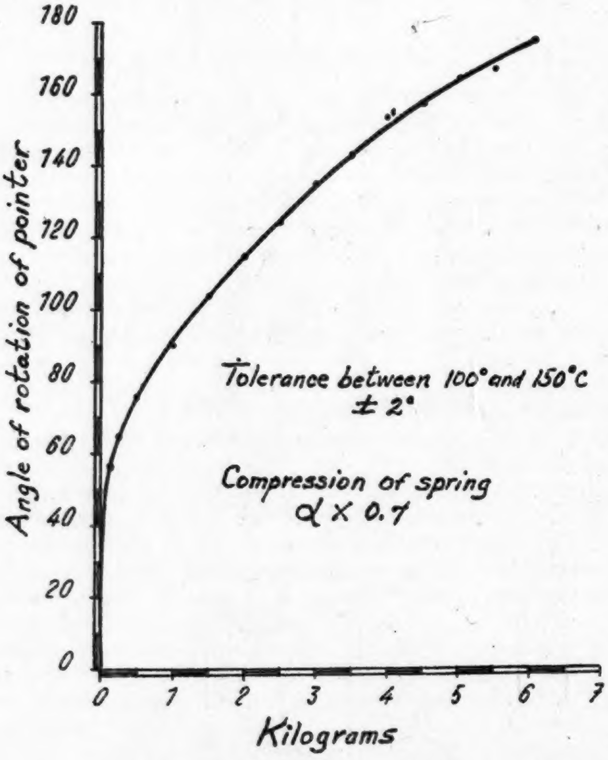

FIG. 3.

The test-specimens were died out from sheets of vulcanized rubber, and had the form and dimensions shown in Figure 4. This form was preferred to the usual circular test-rings, because with such a form it was possible to avoid the sudden change in shape of the rubber ring to conform to the pulley grips when the impact occurred. Also with this special shape, there is a greater proportion of straight section and therefore the elongations and work values are greater.

Static tension tests were then carried out with test-specimens of the same shape as above from each of the rubber sheets; in this case the load was applied by hand and gradually increased. To be certain that any plastic flow had taken place completely, the elongations were not read until ten minutes had elapsed after addition of each load. The elongations were calculated by reading the

distances between the centers of the two pulleys which gripped the test-specimens, both for the unloaded test-specimen and for the same specimen loaded, and then dividing the difference between them by the mean distance of the unloaded test-specimen. In this way there was a small error resulting from the fact that the middle line of the test-specimen was close to the outside surfaces of the grips; this small distance resulted from the decrease in thickness brought about by the elongation. The stress-strain curves obtained under these conditions with various test-specimens from a mixture of 100 parts of maturated ("slab") rubber and 8 parts of sulfur vulcanized in a press for 40 minutes at 3 atmospheres' steam pressure, are shown in Figure 5. Here all curves were found to lie between the two extreme curves shown on the graph. From these curves, by planimetric measurements, were obtained the values of the work of static elongation to predetermined points, as well as the values of the work of rupture.

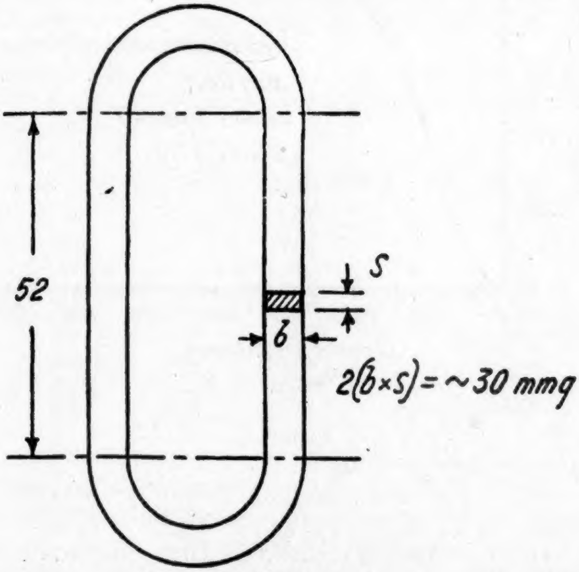

FIG. 4.

The results of static extension were compared with those obtained by the impact method, with no concern for the point of rupture of the test-specimens. The difference between the decrease in potential energy of the falling mass and that absorbed by the spring was therefore the work necessary to elongate the test-specimen to the predetermined elongation.

EXPERIMENTAL RESULTS

Mixture A.—Maturated rubber 100, sulfur 8; vulcanized 40 minutes at 3 atmospheres' steam pressure.

Table I is of real significance, in spite of the fact that the complexity of the tests naturally means that there are minor uncertainties. On the other hand the values which are recorded are the averages of numerous measurements.

It is possible to group the results together to show considerable changes in single variables.

Three conclusions appear evident.

(1) In every case the work expended in reaching any particular elongation is greater when this elongation is reached at high velocity than it is when the elongation is reached at low velocity.

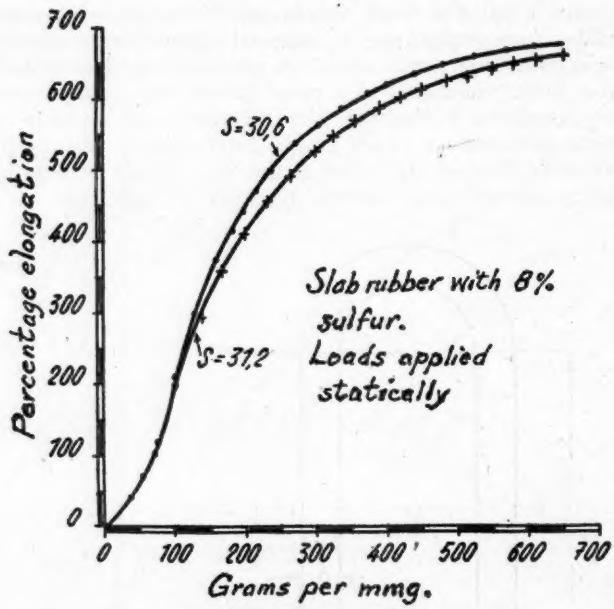

FIG. 5.

TABLE I

H^4 (mm.)	h^4 (mm.)	Velocity V (m. per sec.) at the instant of impact $= \sqrt{2gh}$	Elongation (E) (per cent)	Static work (L_s)	Work of impact L_u (Kg.)	$\Delta L = L_u - L_s$ (kg.)
250	51	1.—	293	0.73	0.78	0.05
300	100	1.41	303	0.76	0.88	0.12
400	201	2	313	0.8	1.1	0.3
450	250	2.23	320	0.82	1.22	0.4
500	300	2.45	325	0.84	1.25	0.41
260	150	1.71	192	0.37	0.48	0.11
350	150	1.71	305	0.78	1.18	0.30
450	150	1.71	411	1.25	1.95	0.7
500	150	1.71	470	1.59	3.4	0.81
300	200	2.0	202	0.32	0.48	0.16
401	300	2.45	216	0.38	0.62	0.24
501	401	2.8	229	0.41	0.68	0.27
350	50	1	408	1.13	1.39	0.26
500	200	2	421	1.27	1.90	0.63

This conclusion seems to be at variance with the hypothesis which was advanced as a logical consequence of the experiments of Williams (*loc. cit.*), and apparently does not conform to the results obtained by van Rossem and Beverdam (*loc. cit.*) with mixtures containing no compounding ingredients.

It should however be noted that these last authors dealt only with the work of rupture, whereas the present author has not reported the results of experiments on the measurement of the work of rupture, because the test-specimens always broke in prefixed positions. Hence there is no justification for assuming that the form of test-specimen plays a decisive part in the rupture, particularly since with static stresses the elongations at rupture are relatively low.

The results of the two eminent Dutch investigators would be at wide variance with those of the present author if it were to be found that rupture takes place at the same elongations. However, there will be occasion to return to this subject later.

In some measurements, negative ΔL values were obtained, but in every case very small absolute values were concerned, and hence it is possible that this result is attributable to experimental errors.

(2) With increase in the velocity at impact, but with a constant elongation at rupture, ΔL increases. At least within a certain interval of time, the latter increase is more rapid than the former.

(3) For a given velocity at impact, ΔL increases with increase in elongation. At least within a certain interval of time, this increase is more rapid than is the increase in elongation.

TABLE II

H	h	V	E	L_s	L_u	ΔL
170	25	0.7	145	1.09	1.70	0.67
250	50	1	160	1.20	2.1	0.9
300	100	1.4	190	1.73	2.9	1.17
350	152	1.72	216	2.23	3.65	1.42
500	250	2.22	255	3.25	5	1.75
250	200	2	110	0.61	1.65	1.04
300	200	2	152	1.17	2.53	1.36
350	200	2	192	1.76	3.35	1.59

Mixture B.—A rubber mixture containing carbon black used for several years for the production of solid tires.[5]

In this series of tests, the spring was removed and the extreme position which the movable grip reached after impact was registered.

In this table the symbols represent the same factors as in Table I.

Without entering into an unnecessarily long discussion of the data in Table II or without comparing in detail the behavior of Mixture A and Mixture B, it should merely be pointed out that the data fully confirm, from a qualitative point of view, the conclusions already drawn.

Curves having as coördinates the velocities at impact and the differences, ΔL, of the work values at a given elongation on the one hand, and curves having as coördinates the elongations and the differences, ΔL, for a given velocity of impact have similar courses. Figures 6 and 7 show in graphical form the data in Tables I and II, but these will not be discussed because it seems advisable at the present time to limit ourselves to a purely qualitative study which will define the fundamental characteristics of the phenomenon in question.

To obtain an idea of the order of magnitude of the elongation at rupture by impact forces, tests were carried out with prismatic test-specimens, for rupture of ring-shaped test-specimens seemed of no particular interest because of differences in tension at various points in the test-specimens.

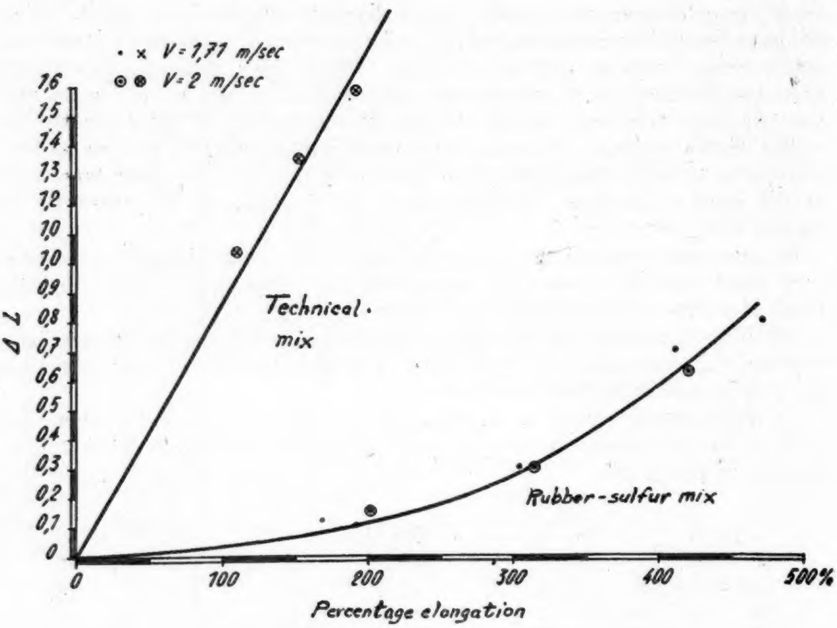
V = 1,77 m/sec
V = 2 m/sec
ΔL
1,6
1,5
1,4
1,3
1,2
1,0
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Technical mix
Rubber-sulfur mix
0
100
200
300
400
500%
Percentage elongation

FIG. 6.

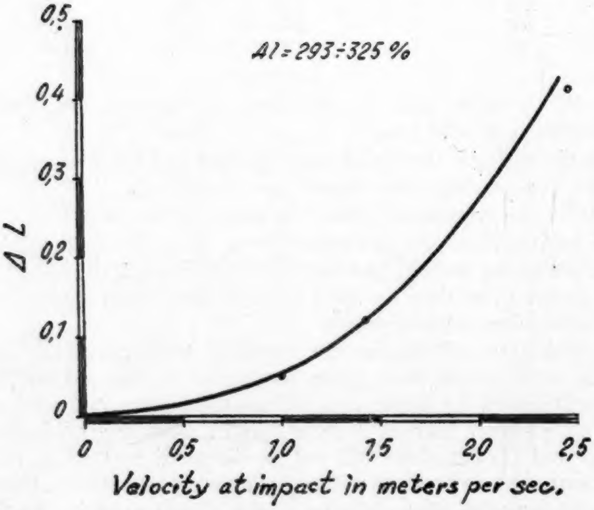
Δl = 293÷325 %
ΔL
0,5
0,4
0,3
0,2
0,1
0
0
0,5
1,0
1,5
2,0
2,5
Velocity at impact in meters per sec.

FIG. 7.

The test-specimens finally used had the form and dimensions shown in actual size in Figure 8. These were tested in a preliminary way to make certain that rupture took place in the middle, where the cross-section was a minimum and was uniform. The thickness was approximately 4 mm.

The jaws were of the eccentric type, with high eccentricity to impart high compression during stretching. In spite of this, the test-specimens tended to slip, not only for this reason but also because the points at which the grips first compressed the test-specimen were displaced, so that the length of the free part of the test-specimen changed during the test. However, only the elongation at rupture or the maximum elongation reached by impact was of interest, and so a correction was made by marks placed on the test-specimens at the elongation chosen.

To allow for this and for numerous other uncertainties, including cutting of the test-specimens, preliminary tare tests were made to correlate the apparent elongations resulting from the changes in distance between the grips with the

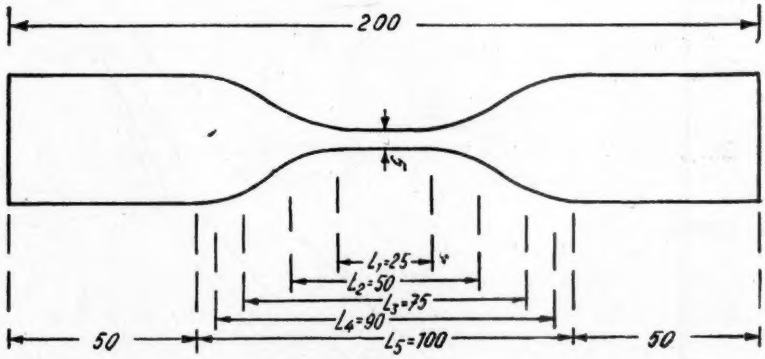

FIG. 8.

elongations actually measured in the center part of the uniform cross-section or at some other point of the same test-specimen (see Figure 9). The path of the falling mass was registered by means of a pointer attached rigidly to it, which marked on smoked paper fastened on a small support (see Figure 10).

The final procedure adopted was as follows. The basket with its weights was allowed to fall from a definite height, which was not great enough to rupture the test-specimen. The height of fall was then increased progressively until rupture occurred. In subsequent tests the weights were dropped from heights a little less than that which caused rupture, and the resulting elongations were measured. The same weights were then dropped from increasingly greater heights onto other test-specimens until a height great enough to cause rupture was reached. The ultimate elongation was however not determined directly in a precise way, and naturally it must have been slightly greater than the highest elongation measured just before the point of rupture.

With the vulcanizate prepared from maturated rubber and 8 per cent of sulfur, the elongations at rupture in no case exceeded 750 per cent, whereas those obtained statically were 825-850 per cent.

One is therefore led to the conclusion that the elongation at rupture is less for impact forces than it is for static forces. This is contrary to the results

obtained by the National Bureau of Standards (*loc. cit.*), which were however not obtained by true and purely impact forces.

When it is considered that the work in reaching a given elongation is greater when expended by an impact force, it becomes evident that, to reconcile the two facts, a not too great difference in the values of the work of rupture must be assumed and that this is at variance with the work of van Rossem and Beverdam. However, the experiments of these latter do not seem to be concerned with pure tension.

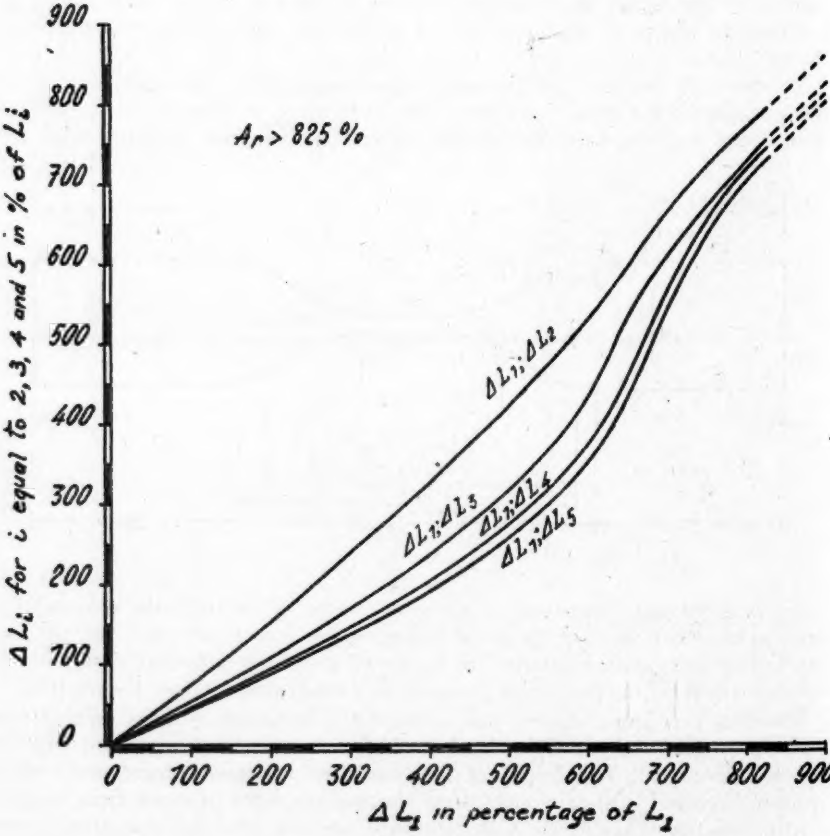

FIG. 9.

It is not safe to affirm, as probably will be agreed, that the investigations cited are comparable, and in any event there are no data to prove it. Nevertheless it would be interesting to gather together a sufficient array of experimental results to settle this point, particularly since, as has been mentioned elsewhere by the present author, the equation which defines the static stress-strain curve of rubber seems to indicate that the parameter which characterizes it most definitely is the elongation at rupture.

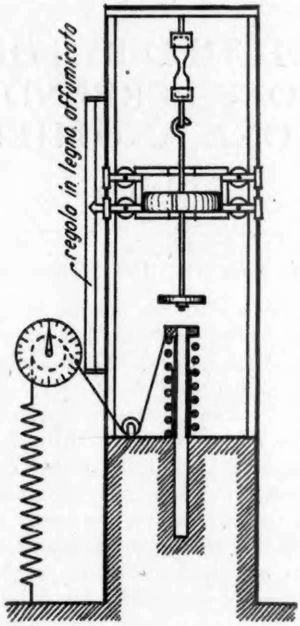

FIG. 10.

RÉSUMÉ

The work of deformation by impact forces acting on a rubber mixture containing no compounding ingredients and on a mixture representative of those used for tires was determined.

It was proved that the work expended in deforming rubber to a given elongation is greater by application of a dynamic force than by application of a static force. The difference between these two values of the work increases with increase in elongation for a given velocity at impact and increases with the velocity at impact for a given elongation.

An attempt was made to determine the elongation at rupture from application of an impact force, from which it was concluded that, at least for mixtures containing no compounding ingredients, this ultimate elongation is less than that reached by the ordinary slow increase in stress.

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[2] Natl. Bur. Standards, Circular No. **38** (1927).
[3] van Rossem and Beverdam, *Rubber Chem. Tech.* **4**, 147 (1931).
[4] The meaning of these symbols is evident in Figure 5. The falling weight was 2.800 kg. in these tests.
[5] It seems useless to give in detail the composition of this mixture, because the idea was not to carry on any systematic work on the relation between resistance to impact and composition, but rather only to prove that the preceding conclusions are valid in general.

RUBBER STRETCHED BY FORCES IN TWO DIRECTIONS PERPENDICULAR TO ONE ANOTHER *

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OBJECT OF THE INVESTIGATION

In previous publications the author has defined by means of relatively simple expressions, the behavior of rubber under tension and under compression. However, as was mentioned in a book entitled "Finite deformations" by the author, it is not possible to develop a theory of elasticity for highly deformable objects, which have their prototype in rubber, unless it is known how they behave when each element is acted upon by the primary three forces which, according to the theory of finite deformations, as well as the ordinary theory of elasticity or again the theory of infinitesimal deformations, are sufficient to define each state of tension. With regard to the last theory, the linear relation between deformation and stress makes it possible to accept the principle of the superposition of simultaneous forces, *i. e.*, to add algebraically all coexistent forces and deformations. However, this is obviously impossible for finite deformations, for which the linear relation in question has not been confirmed.

Rather than proceed on the basis of hypotheses to develop theories and to verify them by deductions, it seemed more reasonable to undertake an experimental investigation, which later would serve as a background for the theoretical development of the problem.

As a beginning, the case of the coexistence of two principal stresses in a relatively thin film has been considered. The experimental results are described in the present paper and will be discussed in a forthcoming paper.

EXPERIMENTAL TECHNIQUE

A moulded test-specimen having the form of a cross was used (see Figure 1). It was stressed in two directions by applying weights by hand on a support connected to the clamp which held the test-specimen at MM, and by means of cords over pulleys (mounted on ball-bearings) these stresses were aligned in the direction NP and the direction LM by weights added successively by hand (see Figure 2).

The tensile stresses in this direction were applied by placing weights simultaneously on the two opposite scales. Allowance was made, after proper taring, for the friction of the moving parts.

The procedure was to maintain constant stresses in the NP direction and then either to increase the stresses gradually in the LM direction or to increase the stresses equally in the two directions.

Since the test-specimens were cut from slabs, their corners had tiny lacerations which made it impossible to carry the measurement to the point of rupture. However, these imperfections had little or no influence on the deformations be-

* Translated for Rubber Chemistry and Technology from *Gomma* (Milano) Vol. 3, No. 2, pages 31-37, March-April (1939).

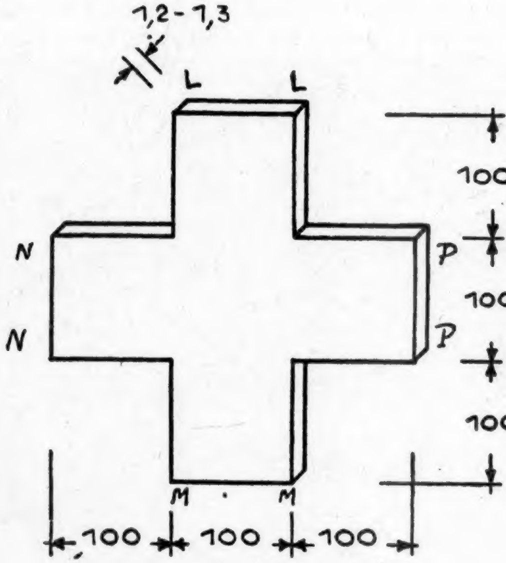

FIG. 1.

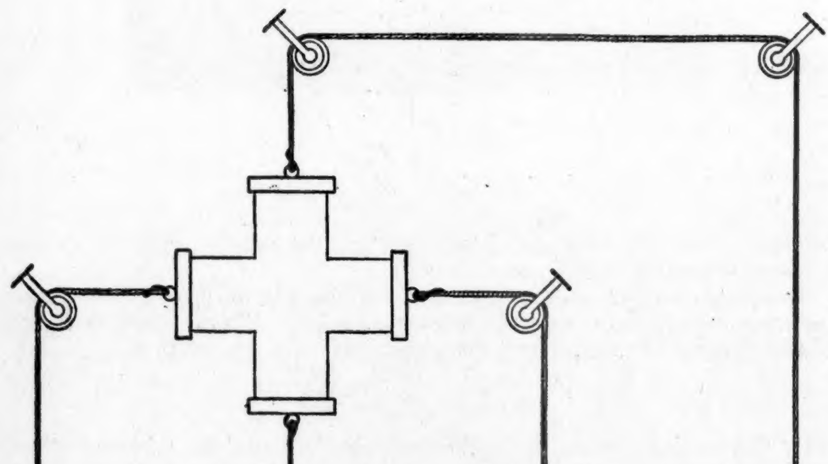

FIG. 2.

low the point of rupture. Also at sufficiently great deformations the test-specimen no longer remained in one plane and the test was therefore meaningless.

The deformations were read on a scale reading in tenths of a millimeter, either along two diameters of a circle previously drawn in the center of the test-specimen or along the sides of a square (see Figure 3) drawn in place of this.

The thicknesses of the test-specimens at their various degrees of deformation were read by calipers graduated in hundredths of a millimeter.

An idea of the distribution of the strains in a test-specimen when stressed in two directions may be had from Figure 4. It can be seen that at the particular deformation in question the sides of the reference square have already become curved. The measurements were made in the positions shown in Figure 3, so that

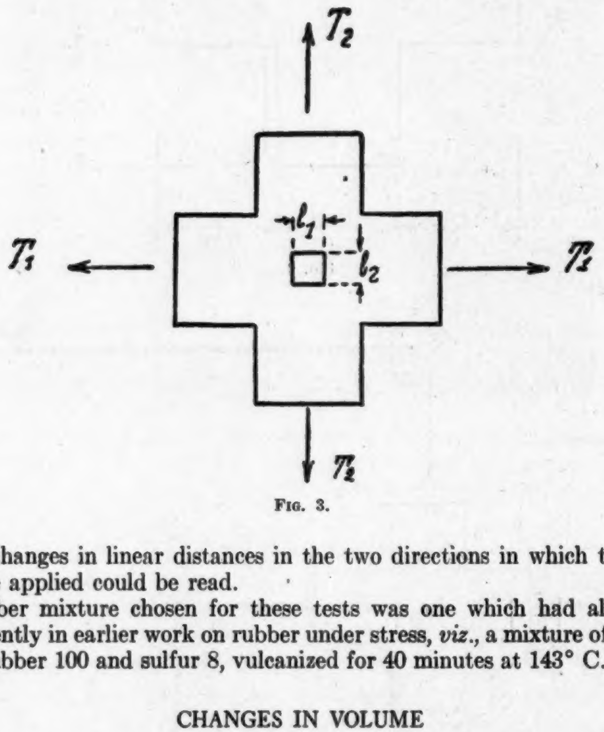

FIG. 3.

the mean changes in linear distances in the two directions in which the external forces were applied could be read.

The rubber mixture chosen for these tests was one which had already been used frequently in earlier work on rubber under stress, *viz.*, a mixture of maturated ("slab") rubber 100 and sulfur 8, vulcanized for 40 minutes at 143° C.

CHANGES IN VOLUME

By determining the lengths in the two directions and the thickness at any particular moment, it was possible to calculate the volume corresponding to any load. Table I gives some results obtained when the loads applied in the two directions were equal.

There was perhaps a tendency for the volume to diminish somewhat when the rubber was deformed but the changes were not significant. The mixture used in the tests was of the type which contained no compounding ingredients, and with which no change in volume was found during simple extension tests.

CHARACTER OF THE STRESS-STRAIN CURVES

Figure 5 reproduces the stress-strain curves for direction (b) for various loads T_1 acting in direction NP.

FIG. 4.

TABLE I

Sample	Load (kg.)	Length in two directions * (mm.) (a)	(b)	Thickness (mm.)	Volume (cc.)
I	0	30	30	1.2	1080
	5.7	35.5	37.5	0.8	1065
	8.9	42	46	0.55	1062
	12.1	53.5	56.5	0.34	1028
	15.3	63	68	0.25	1071
II	0	30	30	1.2	1080
	2.5	31	34	1	1054
	5.7	37	39	0.73	1053
	8.9	44	48	0.51	1077
	12.1	54	59	0.33	1051
	15.3	66	71	0.2	937

* Direction (a) is direction NP in Figure 3: the length is indicated by l_1 in Figure 3. Direction (b) is direction LM in Figure 2; the length is indicated by l_2 in Figure 3.

Both T_1 and T_2 are expressed in grams per sq. mm. of the original cross-section. This section was calculated by multiplying the initial thickness (approximately 1.3 mm.) by the widths LL and NN of the two arms of the test-specimen.

Figure 5 also shows the stress-strain curve for stresses in a single direction ($T_1=0$), and a comparison between it and the other curves shows that applica-

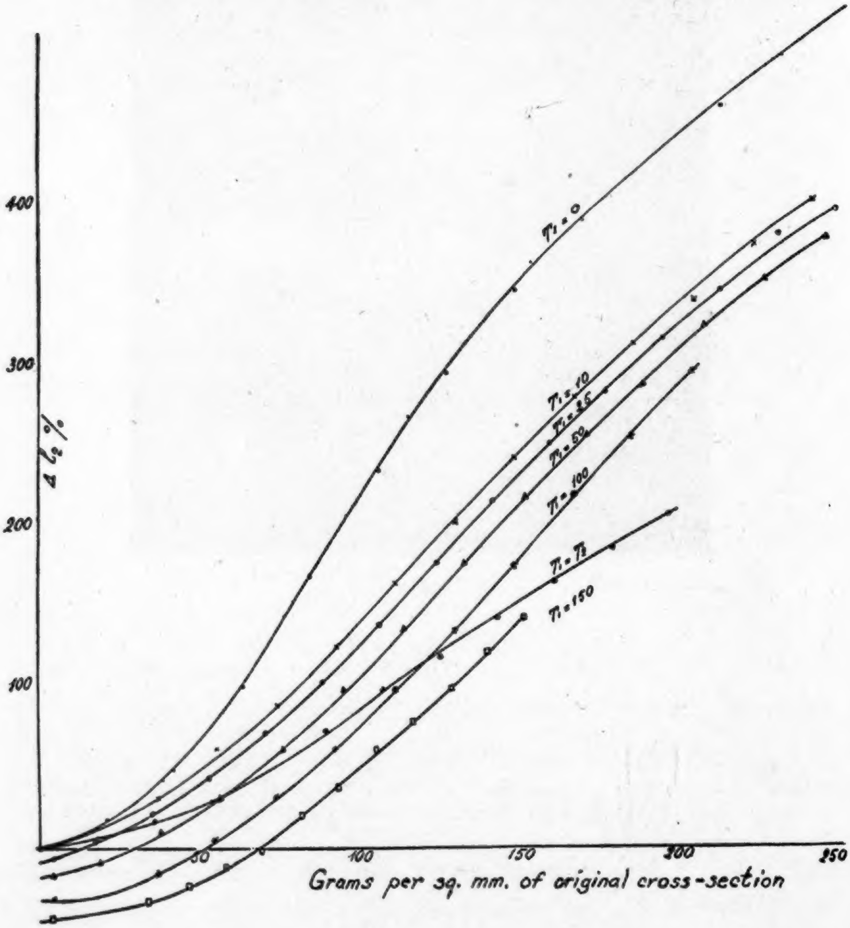

FIG. 5.

tion of tension T_1 did not alter the qualitative character of the stress-strain curve in direction (b); this was always S-shaped, but was straightened by application of stress T_1. In substance this stress acted like a reënforcing ingredient.

It is well to point out here that, according to the theory of infinitesimal deformations, with ε (the elongations) and σ (the Poisson coefficient) given, the following relation must be valid:

$$T_2=E(\varepsilon_2-\sigma\varepsilon_1)$$

where E is the modulus of elasticity. Hence with application of stress T_1 not only does the linear relation between the stress and deformation still hold, but also the slope of the line is maintained, the latter being merely displaced parallel to itself.

It should also be noted that the curve formed by changing both stress T_1 and stress T_2 simultaneously is noticeably less steep on the stress axis of the other curves. Moreover the elongation for a T value where $T_1=T_2$ is in every case slightly greater than that on the curve for $T_1=T$, corresponding to the abscissa $T_2=T$.

Most of these facts are perhaps self-evident, but it seemed a good idea to verify them experimentally.

To base the forces on unit "actual cross-section", the thickness was determined directly, in some cases on the assumption that the volume remained constant during the deformation, whereas the other dimension of the cross-section was determined by direct measurement.

The stress-strain curves which were obtained in this way, and which correspond to those in Figure 5, are reproduced in Figure 6. At least from the qualitative point of view, it is evident that their form has not been changed by the effect of transverse stress, but that this stress stiffens the test-specimen a little and straightens the stress-train curve, and finally that the curve representing the coexistence of two tangential stresses perpendicular to one another and equal in value is slightly inclined to the horizontal of those representing a variable stress and constant stress.

In view of the approximate parallelism of the curves of different T_1 values, it may be considered that, between the limits of approximation of the measurements, they are displaced only at the origin, *i. e.*, they differ only in that the initial lengths ($T_2=0$) are different. If so, the equation:

$$y_{T1}=f_{T1}(x)=f_{T'1}(x)+constant.$$

may be accepted as a first approximation. The significance of the symbols is obvious. However, this relation should not be extended to the point where $T_1=0$, and it is essentially different from the case of infinitesimal deformations.

As for the stress-strain curve, when the external force acts in only one direction, it has already been shown in earlier work that the following equation is valid:

$$xy+bx+cy=0$$

where x is the unit force referred to the actual cross-section, y is the coefficient of the corresponding distension, and b is a negative value which in no case can be exceeded by the elongation at rupture. The ratio: b/c, is the slope of the elongations on the axis at the beginning of the curve.

The question is then what equation represents the curves for stress in two directions when in one of these directions the stress T_1 is maintained constant. This equation is in reality the same, as shown by the data in Table II, in which the values of b and of c introduced into the calculations in the cases indicated and some values of y calculated from given values of x (T_1 refers to the original cross-section), provided however that to the registered elongation is added the contraction resulting from application of the force in the perpendicular direction T_1..

This elongation is 0.22 (*i. e.*, 22 per cent) for a T_1 value of 50, 0.38 when T_1 is 100 and 0.46 when T_1 is 150. For example, in this last case, the equation is:

$$x(y+0.46)+bx+c(y+0.46)=0.$$

The values recorded for this initial elongation coincide very well with the curves in Figure 6.

This is therefore a confirmation of the parallelism described above, since the b values and c values are practically equal for the three values of T_1 under consideration. It should be noted also that the c constant is equal to that for a stress in a single direction, whereas b is greater for this condition. This fact is in its

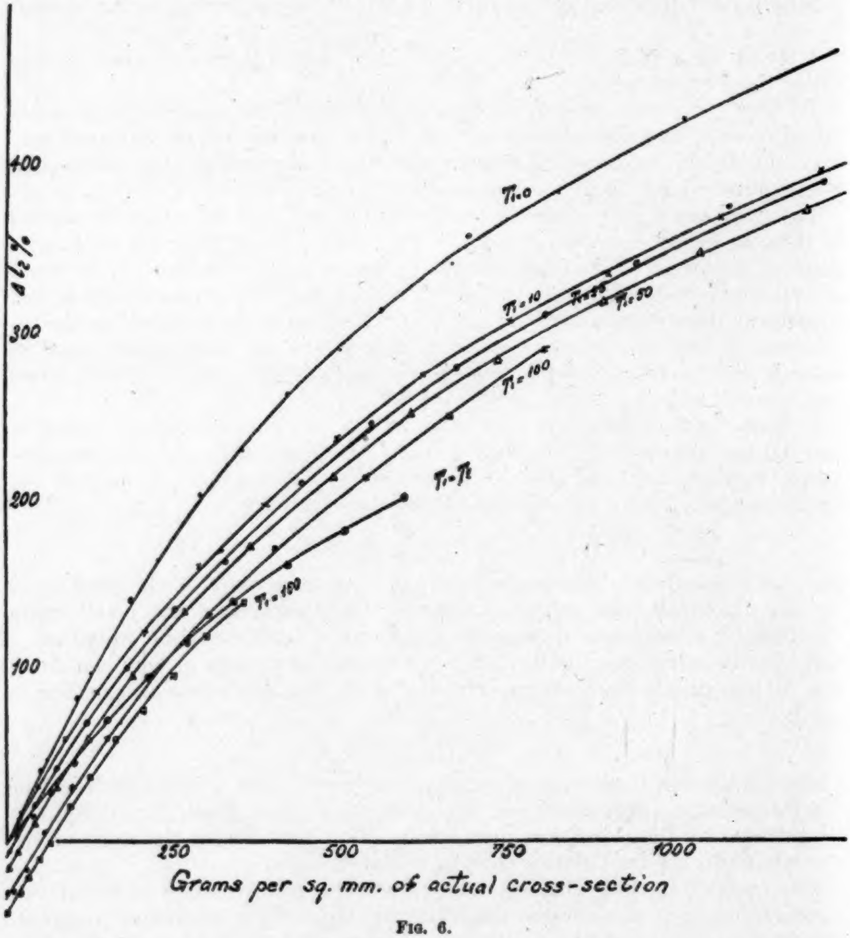

FIG. 6.

turn in accord with the closer proximity to the axis of the deformations of the curve corresponding to $T_1=0$ compared to the proximity of the others.

Hence it is still possible to consider the deformations as additive, provided that account is taken of the fact that one of the variables changes rapidly in passing from a test-specimen stressed in only one direction to a test-specimen stressed in two directions. With the interpretation given to b for simple tension, this means that very probably the addition of a transverse stress diminishes the total maximum elongation attainable in the longitudinal direction (that of T_2).

The next problem is to derive the equation concerned with the simultaneous application of the two stresses T_1 and T_2. In this case the stress T_1 (when referred to the cross-section of the test-specimen deformed by this stress this will be designated t'_1) may be assumed to be applied first. Consequently the resulting deformation, whose coefficient of expansion (for simple extension) is y_1, is represented as follows:

$$y_1 = \frac{-b_1 t'_1}{t'_1 + c} \tag{1}$$

Accordingly the contraction in the direction of T_2 and in thickness is defined by the coefficient $\sigma_1 y_1$, where y_1 is the value of the function which replaces the coefficient of Poisson for the y_1 value of the expansion[1].

TABLE II

X (g. per sq. mm.)	$T_1=0$; $b=-8$, $c=900$; y Calculated	Found	$T_1=50$ (g. per sq. mm.); $b=-7$, $c=900$; y Calculated	Found	$T_1=100$ (g. per sq. mm.); $b=-6.9$, $c=900$; y Calculated	Found	$T_1=150$ (g. per sq. mm.); $b=-6.8$, $c=900$; y Calculated	Found
50	0.40	0.42	0.15	0.15	0.02	0.017	0.12	0.098
100	0.78	0.80	0.49	0.48	0.31	0.31	0.21	0.22
200	—	—	—	—	0.875	0.875	0.78	0.78
300	2.08	2	1.64	1.53	1.34	1.34	1.21	1.21
500	2.92	2.96	2.28	2.28	2.08	2.08		
600	3.26	3.2	2.57	2.58	2.37	2.38		
700	—	—	—	—	2.64	2.64		
800	3.80	3.76	3.07	3.07				
900	—	—	—	—				
1000	4.23	4.21	3.51	3.46				
1100	4.40	4.40	3.71	3.73				

Application of stress T_2 therefore brings about a deformation in the direction of its application, and this is defined by the following expression:

$$t_2(y_2 + \sigma_1 y_1) + b_2 t_2 + c(y_2 + \sigma_1 y_1) = 0 \tag{2}$$

where t_2 is the stress referred to the actual section in that direction.

Suppose now, for simplification, that there is no change in volume with the particular rubber mixture concerned, as actually is true of rubber-sulfur vulcanizates and is approximately true of other mixtures which are not loaded with inert ingredients.

In such a case[1]:

$$t'_1 = \frac{T_1}{(1 - \sigma_1 y_1)^2}$$

and therefore:

$$\sigma_1 y_1 = 1 - \sqrt{\frac{t'_1}{T_1}} \tag{3}$$

To write the final equation, it is necessary to know how t'_1 changes, *i.e.*, the stress referred to the unit cross-section of the test-specimen deformed only by stress T_1, when the basis of reference is changed to the unit cross-section of the test-specimen deformed by stress T_1 and stress T_2 simultaneously. Now the

deformation caused by stress T_2 brings about an elongation of the coefficient y_2 in the direction of stress T_2. In the direction of the thickness of the test-specimen it would appear logical to assume, on the basis of symmetry of effects, that the first (y_1) deformation and the second $(y_2+\sigma_1 y_1)$ deformation are such that the effect is that of a single deformation $(\gamma_1+\gamma_2+\sigma_1\gamma_1)$ in one of the two directions in question.

Therefore the thickness[2], which after the first deformation was equal to $1-\sigma_1\gamma_1$, where

$$\sigma_1=\frac{1}{2y_1+1.25}$$

becomes after the second deformation:

$$1-\sigma_2(y_1+y_2+\sigma_1 y_1)$$

where

$$\sigma_2=\frac{1}{2(y_1+y_2+\sigma_1 y_1)+1.25}$$

As a final result, therefore, the application of stress T_2 changes the cross-section on which stress t_1 acts from unity to:

$$S_{1,2}=\frac{(1+y_2)[1-\sigma_2(y_1+y_2+\sigma_1 y_1)]}{1-\sigma_1 y_1}$$

and therefore the actual unit stress in direction T_1 becomes:

$$t_1=\frac{t'_1(1-\sigma_1 y_1)}{(1+y_2)[1-\sigma_1(y_1+y_2+\sigma_1 y_1)]}$$

$$=\frac{T_1}{(1+y_2)(1-\sigma_1 y_1)[1-\sigma_2(y_1+y_2+\sigma_1 y_1)]}$$

The problem is therefore solved; in fact from equations (1), (3) and (4) it is possible to derive y_1, σ_1 and t'_1 as functions of the constants b_1 and c, which refer to the resistance of the rubber being tested under stress and to the external stress T_1. Equation (2) reduces then to a relation between t_2 and y_2 on the one hand and the constants on the other, a relation of hyperbolic character. Finally from equations (5) and (6), tension t'_1 can be calculated.

A solution of the system of equations just derived has not been attempted, because it is evident that they do not represent simple relations which can be interpreted directly. Rather they have been derived to show how highly complex they are.

The character of the curves obtained experimentally indicates that they are hyperbolic, the equations of which have coefficients different from those representing simple deformation.

RELATION BETWEEN THE COEFFICIENT OF EXPANSION IN THE DIRECTION OF STRESS AND THAT OF CONTRACTION PERPENDICULAR TO THIS DIRECTION

Since formula (5) derived above was of service in formulating simple hypotheses, it should be a general expression of the phenomenon. This can in fact be verified in a few simple cases.

Let T_1 be constant at 50 grams per sq. mm., while T_2 changes. From Tables I and II is obtained a value of y_1 of 0.22 and σ_1 is calculated to be $\sim$0.60. Hence Equation 5 becomes:

$$\sigma_2 = \frac{1}{2y_2 + 1.95}$$

The changes in σ therefore remain identical with those for stress in a single direction, but the constant which appears in the denominator, becomes a function of T_1.

TABLE III

Coefficient of expansion (D) in the directions (a) and (b)	Coefficient of Contraction (C)	$\sigma = \frac{C}{D}$
0.166	0.257	1.55
0.293	0.386	1.32
0.47	0.53	1.13
0.73	0.67	0.92
0.98	0.745	0.76
1.18	0.79	0.67
1.43	0.83	0.58
1.65	0.856	0.52
1.85	0.876	0.47
2.06	0.893	0.44

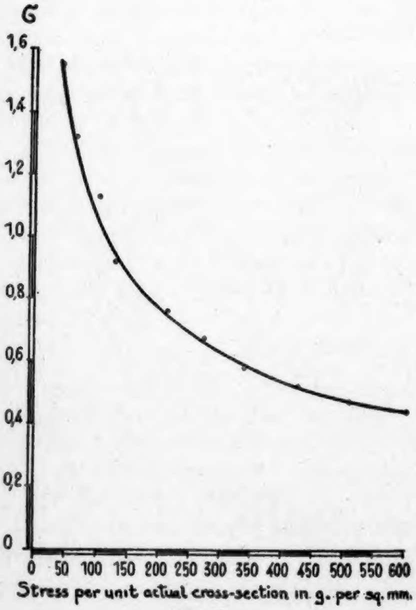

FIG. 7.

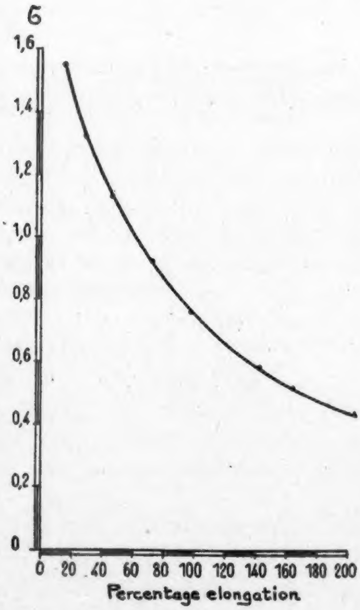

FIG. 8.

On the other hand, if equal deformations are maintained in the two directions (a) and (b) the values recorded in Table III are obtained.

Figures 7 and 8 give the values of σ as a function of the elongations in the two directions or of the stresses per unit actual cross-section which are applied in

the same directions as those in which they are measured. The changes are roughly those corresponding to simple tension in one direction.

It is therefore readily proved that a relation such as that derived previously is not adapted to represent the phenomenon in the present case.

RÉSUMÉ

The results of tests, in which suitable samples of vulcanized rubber containing no compounding ingredients were stretched simultaneously in two directions, perpendicular to one another in the same plane, are described. It was found that the volumes remained practically unchanged while the test-specimens were being deformed.

The course of the stress-strain curve obtained by maintaining the stress constant in one of the two directions and varying the stress in the other direction was identical to the course of the course of the curve obtained with a stress in only one direction, except for changes in the values of the constants in the equation which represents this single stress.

The theoretical complexity involved in the application of stress simultaneously in two directions is demonstrated, and it is also pointed out that certain relations which are true of simple extension do not hold true of stresses in two directions.

The general nature of the stress-strain curves and of the curves which express the relation between change in thickness and elongation as a function of the deformation are described.

REFERENCES

[1] With reference to this function, see a paper by the author entitled: "The resistance to stress of vulcanized rubber". Notes I and II. *Nuovo cimento* **1925** and **1927**.

[2] The reader is referred to Note II of the article by the author, entitled "The resistance to stress of vulcanized rubber", *Nuovo cimento* **1927**.

RELATIONS BETWEEN VULCANIZATION AND REINFORCEMENT *

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The increasingly effective use of commercial rubber products in various fields has been due in large measure to improvement in the techniques of vulcanization and reinforcement by powders. The thinking and experimentation along these two lines have, in the main, treated the two subjects separately, and there have appeared to be few obvious points of close contact between them. The literature treating the relations between vulcanization and reinforcement is limited to a few publications.

There are, however, certain respects in which reinforcement and vulcanization may be compared or related and in which their effects should be studied simultaneously. The purpose of this paper is to consider these possible relations of vulcanization and reinforcement from the points of view indicated by the following questions:

1. What degree of similarity exists between powder reinforcement and vulcanization as judged by the effect on the physical properties of the mix, and may vulcanization be considered to be a pigmentation effect?
2. Are permanent changes in the character of the rubber hydrocarbon induced by addition of finely divided powders, and is this effect similar to the change produced by vulcanization?
3. Are the abnormal effects on the stress-strain curve of vulcanized rubber produced by small quantities of zinc oxide similar to the effects produced by addition of larger quantities of finely divided powders?
4. What are the effects of reinforcing powders on the rate of vulcanization?

The subjects are placed in the form of questions for emphasis rather than to suggest the hope in all cases of direct and decisive answers.

RUBBER-SULFUR COMPLEXES

A number of years ago it was suggested[26, 31, 35] that, during the course of vulcanization, rubber-sulfur complexes were formed in uniform distribution throughout the rubber mix and that these units, being of extremely small dimensions, influenced the rubber in much the same way as would additions of finely divided reinforcing powders.

In order to compare the effects of pigmentation and vulcanization in this particular light, the following stocks were compounded (in parts by weight):

	A	B	C	D	E	F	G
Rubber	100	100	100	100	100	100	100
Channel gas black	—	1.9	9.5	19	38	57	76
Sulfur	6	—	—	—	—	—	—
Vols. of pigment	—	1	5	10	20	30	40

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 31, No. 11, pages 1402-1406, November 1939.

Stock A was cured in a press at 140° C for 10, 20, 30, 60, 90, 120, and 180 minutes. The uncured stocks containing carbon black were hot-pressed into suitable form for testing and compared with the various cures of stock A in regard to modulus, tensile strength and resilience. In the case of plasticity, unpressed stocks were used.

Tensile and modulus results at 500 per cent elongation were obtained on the Albertoni machine and are shown in Figure 1. It is evident that, although both treatments have affected the rubber in the same direction, the effect of adding channel gas black over the normal loading range has been more marked than that of cure over the usual curing range. This is especially noticeable in the case of modulus. There is also a greater tendency to reduce the elongation and move

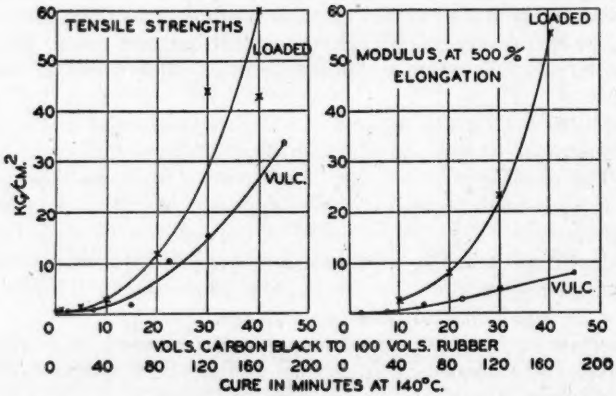

FIG. 1.—Tensile strength and modulus of vulcanized and loaded stocks.

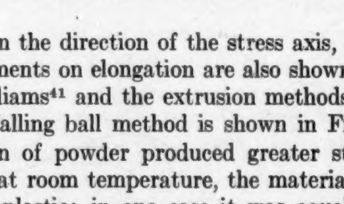

FIG. 2.—Stress-strain curves of vulcanized and loaded stocks.

the stress-strain curve in the direction of the stress axis, as Figure 2 shows. The effects of the two treatments on elongation are also shown in Figure 3. Plasticity results by both the Williams[41] and the extrusion methods[8] are given in Figure 4. Energy return by the falling ball method is shown in Figure 5.

Although the addition of powder produced greater stiffness as measured by stress-strain properties at room temperature, the material containing the powder was much more thermoplastic; in one case it was equal in flow characteristics and in the other it was easier to extrude at the higher temperatures used than the cured stock at comparatively low states of vulcanization. This is further illustrated by the extruded stocks shown in Figure 6. It is apparent that stock E containing 20 volumes of channel gas black extruded more smoothly than even the low cures of stock A, in spite of its much higher modulus.

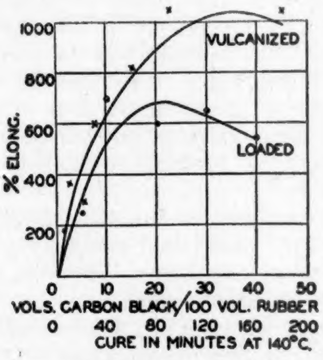

FIG. 3.—Elongation of vulcanized and loaded stocks.

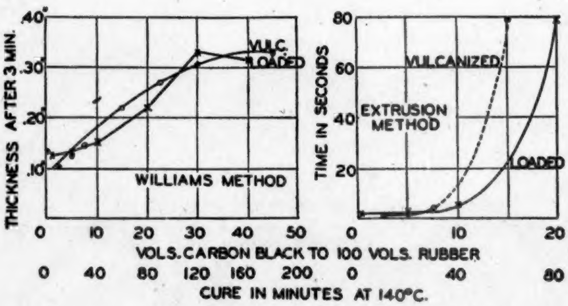

FIG. 4.—Plasticity of vulcanized and loaded stocks.

Williams method: temperature, 80° C.; volume of pellet, 2 cc.; load on plate, 5 kg.
Extrusion method: time in seconds for extrusion of 5.65 cc. at 107° C. No extrusion of the vulcanized stock took place at the 60-minute cure; the time values are as high as or higher than are indicated by the curve.

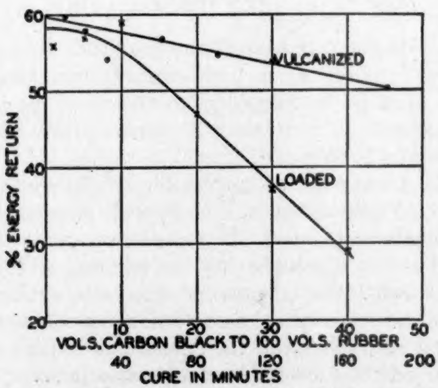

FIG. 5.—Energy return of vulcanized and loaded stocks.

The data given must be considered as little more than an introduction to the subject and suggestive only. Limitations of time have prevented the more thorough comparisons which the subject seems to warrant. Work at low temperatures might throw further light on the degree of relation between the two effects. The scanty nature of the available data makes it difficult to draw definite conclusions. The indications are that vulcanization is not to be interpreted as an effect similar to that produced by fine powders. Similar conclusions were drawn by Garvey[12].

The formation of sulfur linkages, which is the classical and generally accepted view of the chemistry of the vulcanization process, was long considered an adequate explanation of the physical changes. When the work of Williams[42, 44] is considered, this view seems no longer tenable.

To date we have no wholly adequate and well substantiated explanation of the physical changes occurring during vulcanization[3, 13, 14, 15, 23, 24, 27, 33, 43]. Any further discussion of this point, however, is beyond the scope of the present paper.

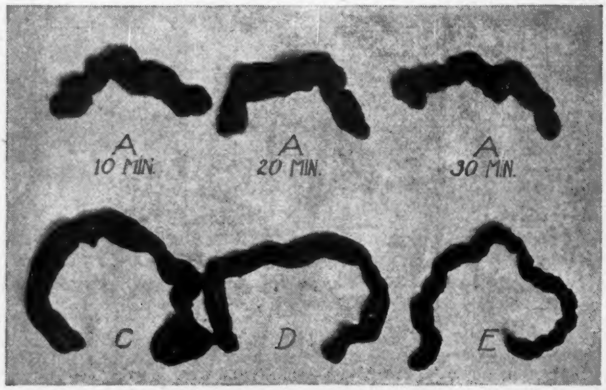

Fig. 6.—Extruded stocks.

PERMANENT CHANGES IN RUBBER HYDROCARBON BY PIGMENTATION

Frequent references have appeared in the literature to the effect that many powders when milled into rubber in high concentration and in the absence of vulcanizing agents produce a change in the physical properties of the mix similar to those brought about by premature vulcanization. The phenomenon was reported many years ago by Weber[37].

It is well known that when the volume loading of the powder exceeds a certain minimum in a carbon black-rubber mix, it appears impossible to remove all of the rubber by benzene extraction[16]. This behavior appears to be closely related to the changes produced in the rubber by the addition of magnesium carbonate and other pigments which Menadue[22] described as being similar to those produced by vulcanization. (The increase in refractive index of rubber on addition of powders might be thought related to the above observations were it not for the fact that the rubber resumed its original refractive index upon removal of the powders. It should be noted that this method of examination is limited to very low powder concentrations[19].)

The nature of the effect observed has never been further elucidated although the experiments have been verified in certain respects[5].

It is known that, in the case of channel gas black-rubber mixes, flocculation takes place during the stiffening process[25] which accompanies heating of the mix.

Measurements on liquid paraffins at room temperature demonstrated[4] that marked increases in surface tension accompany the introduction of fine powders; this indicates the presence of strong cohesive forces between particles.

Although such forces may account for part or all of the increase in stiffness of the rubber powder batch, this does not constitute an acceptable explanation of the above-mentioned partial retention of the rubber by the powder mix during extraction with solvents, nor does it account for the stiffness and insolubility of the rubber residue obtained by removal of the powder. Neither do the concepts of Depew[7] or Wiegand[38] appear to account for this phenomenon. The former postulates a structure similar to a semipermeable membrane. The latter conceives of the rubber as macromolecules with the pigment held in the interstitial spaces.

Although Menadue hinted that the effects noted by him may be caused by oxidation, he did not seem inclined to consider this explanation very seriously.

Dufraisse[6] in his review of the effect of oxygen on rubber showed evidence that under proper conditions oxygen can produce results similar to those produced by sulfur—in other words, stiffening in the case of raw rubber and gelation in the case of solutions.

It is hardly to be doubted that oxygen is adsorbed on the surfaces of all the pigments used by Menadue, and it is possible that the unique conditions necessary for so-called oxygen vulcanization may exist at these surfaces. Spence and Ferry[30] also pointed out that "a number of oxidizing agents can build up or break down the polymeric structure of rubber depending on the conditions of treatment".

The recently discovered power of cellulose[32] as an agent for inducing oxidation of rubber has been demonstrated in the production of certain commercial products. The oxidizing effect was obtained simply by mixing on the mill. Other materials were also reported as having limited activity—for example, kieselguhr, slate, dust, powdered asbestos, etc. When heated out of contact with air, these products are reported to change to a tough, nontacky gel similar to polymerized wood oil.

It seems possible in the light of the above facts that the introduction of powders into rubber on the mill may produce slight oxidation of such type as to effect an increase in the size of the molecular units of rubber and thus account for the phenomenon noted by Menadue.

This discussion suggests that the change in physical state of the rubber hydrocarbon induced by addition of certain powders may be the same in character as that produced by vulcanization, both being types of aggregation accompanying in one case the combination of the rubber hydrocarbon with oxygen and in the second case combination with sulfur. This statement is not to be interpreted as meaning that combination with oxygen is always accompanied by the physical changes noted by Menadue, nor is there any implication that the effect of fine reinforcing powders is due wholly to oxygen vulcanization.

Although the data at hand are not sufficiently convincing to warrant a definite conclusion, they indicate the necessity of reconsideration of the problem. Repetition of some of the above work and examination of some of the products by more rigorous testing methods should throw new light upon the subject.

ROLE OF ZINC OXIDE IN CURING

Dinsmore[9] showed that one volume of zinc oxide added to a rubber-sulfur mix increases the modulus of the mix almost twice as much as does one volume of channel gas black. A check run was recently made in which the above comparison was repeated and several other variables were added. The stocks tested were as follows (in parts by weight):

	E	F	G	H	I	J	K
Acetone-extd. pale crepe [a]	100	100	100	100	100	100	—
Smoked sheet	—	—	—	—	—	—	100
Zinc oxide	—	—	6	6	6	—	6
Carbon black	—	1.9	—	—	—	9.5	—
Stearic acid	—	—	—	1	5	—	—
Sulfur	6	6	6	6	6	6	6

[a] Residual acetone extract, 0.45%.

A series of cures was made at 143.5° C. (290° F.), and the stress-strain relations of the 120-minute and 180-minute cures are shown in Figure 7. When

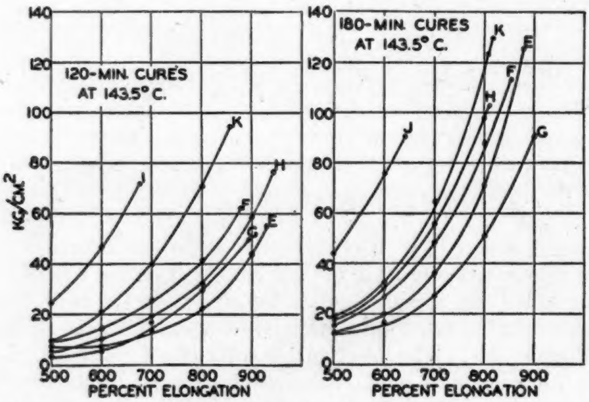

FIG. 7.—Stress-strain curves showing effect of zinc oxide and stearic acid compared with that of carbon black.

cured for 120 minutes, the stress-strain curves of both the zinc oxide, G, and the carbon black stock, F, are higher than that of the control, E. The carbon black stock is stiffest, as would be predicted on the basis of the known reinforcing behavior of the two powders. When 1 part of stearic acid is added to the mix, H, a slight increase in the stress-strain curve of the zinc oxide stock occurs; when 5 parts of stearic acid are added, I, the curve for zinc oxide is considerably higher than the curve for the carbon black mix. Stock made from natural rubber, K, occupies the expected intermediate position and checks the result reported by Dinsmore. The general trend is the same in the case of the 180-minute cures except that the zinc oxide stock, G, was actually lower than the control. The addition of 1 part of stearic acid in this case raised the zinc oxide stock above the carbon black stock. It is evident that the abnormal stiffening produced by the addition of zinc oxide in mixes containing only natural rubber and sulfur is not a matter of powder reinforcement.

Further data relative to the comparative effects of the various single agents required in combination for satisfactory cure of accelerated stocks are shown in Figure 8. The stocks tested were as follows (in parts by weight):

Stock no.	49	50	51	52	53	80
Rubber	100	100	100	100	100	100
Sulfur	6	6	6	6	6	6
Stearic acid	—	3	—	—	3	3
Zinc oxide	—	—	5	—	5	5
Mercaptobenzothiazole	—	—	—	1	1	—

Times of cure and coefficients of vulcanization determined by the Kelly method[20] are shown in Figure 8. Although the addition of stearic acid to a rubber-sulfur mix has an adverse effect on the stress-strain curve, the addition of zinc oxide produced again in this case a marked movement of the stress-strain curve toward the stress axis; and in the presence of additional stearic acid this move-

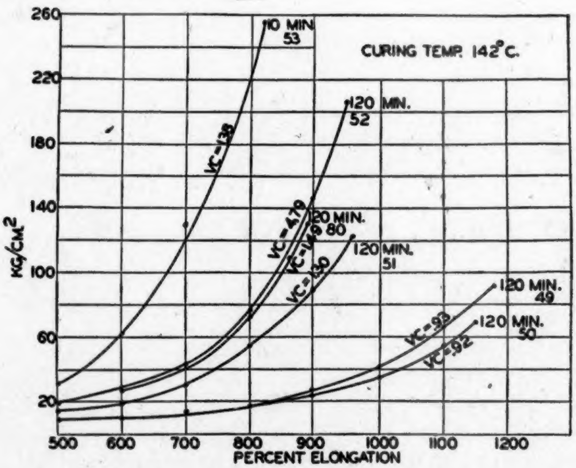

FIG. 8.—Stress-strain curves showing effect of zinc oxide and stearic acid compared with that of accelerator.

ment is almost as great as that produced separately by the accelerator alone. It is of interest to note that the change in position of the stress-strain curve has been produced by the zinc oxide with a comparatively small change in the amount of sulfur combined. This fact was also pointed out by Beadle and Stevens[1] and by Kelly[20].

The stiffness increases obtained by Williams[43] on addition of zinc propionate to cured rubber-sulfur stocks are even more striking evidence of the activity of zinc oxide in rubber mixes than the data presented above. The fact that low zinc oxide stocks can be made which are optically clear is abundant proof of the reaction that takes place between zinc oxide and fatty acids or other substances in the mix.

In view of the knowledge that certain of the metallic stearates form definite gels in hydrocarbon media, it might be suggested that the zinc salt which is undoubtedly formed is precipitated during or immediately after vulcanization in the form of a gel or suspension; since it is fixed in the matrix of vulcanized

rubber, it behaves in somewhat the same manner as a very fine reinforcing powder. The result obtained in the case of stock 53 may thus include the separate effects of zinc stearate and accelerator which are shown in the above-mentioned stress-strain curves and which thus contribute to the total result.

The literature provides scanty substantiating evidence for the suggested explanation, and ten years after Dinsmore's work[9] there is little progress to report in the solution of this problem. However, in view of our lack of knowledge of the fundamental nature of the change induced in rubber by the union with sulfur, there is slight cause for wonder that we are unable to explain the evidently more complicated effect produced by zinc oxide and fatty acids.

Little effort has been directed to experimental work which would clearly explain the behavior of zinc oxide separately from its effect on accelerators. A thorough study of this field would doubtless furnish valuable information regarding the causes of the physical changes which take place during vulcanization.

EFFECT OF REINFORCING PIGMENTS ON RATE OF VULCANIZATION

Among the early investigations of the effect of powders on the rate of vulcanization is that of Thies[34]. This work indicated a decided effect of various clays on rate of vulcanization, and the effect was shown to parallel adsorptive capacity. Although Thies noted that the clays were not neutral, pH was not eliminated as a variable. Later Winkleman and Croakman[45] indicated the importance of acidity and alkalinity in regard to curing effects in the case of clays.

A number of detailed studies have been made comparing the adsorptive qualities of various carbon blacks and the retardation of rate of cure which they induced in a rubber mix. Data in certain papers[10, 11, 16, 29, 36, 39] were, in general, interpreted as indicating a relation between adsorptive capacity of black and its effect upon curing rate. There were some anomalies, however, which remained unexplained; indeed Le Blanc, Kröger, and Kloz[21] could find no such relation.

Other investigators[2, 17, 18, 28], dealing more directly with the chemical constitution of the carbon black, established a relation between oxygen content and effect on rate of vulcanization; they appear to show that, although adsorption may play a definite part, its effect is subordinate to that of oxygen content.

However, it seems that the authors cited have been debating a nonexistent problem if the first several pages of a recent paper by Wiegand and Snyder[40] are to be taken at face value. These writers claim that carbon blacks accelerate rather than retard the cure. Whether or not we agree with these authors in this particular conclusion, the main portion of the paper relating curing rates and pH of various carbon blacks in water suspension marks a distinct step forward in our understanding of the effect of reinforcing powders on rate of vulcanization. They indicate in what manner the adsorption of accelerators and activators is dependent on the oxygen content of carbon black and thus reconcile the apparently conflicting views presented above. In view of the complicated nature of the subject, it is scarcely to be expected that the views and conclusions of these latter authors will stand unchallenged in all details. The basic ideas, however, form a working hypothesis upon which further research may be grounded.

SUMMARY

1. It seems unlikely that the effects of vulcanization are due to reinforcement produced by discrete rubber sulfide particles and due to their fineness and state of dispersion.

2. There seems to be some indication that the changes which result from the introduction of finely divided powder are due to oxidation of the rubber hydrocarbon. The final products, both chemically and physically, are analogous to rubber-sulfur compounds.

3. The peculiar behavior of zinc oxide when added to rubber-sulfur mixes indicates that this material reacts during vulcanization and produces reinforcing effects of a magnitude not to be explained by its particle size and not dependent on the presence of added organic accelerator.

4. The latest information regarding effect of powders upon rate of vulcanization indicates that differences among powders in this respect are due to differences in adsorption. These latter differences result from the nature of the powder surface, which affects adsorptive power in such a way as to make its action preferential to certain constituents in the mix.

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A NEW METHOD OF INVESTIGATION IN THE EVALUATION OF FILLERS FOR THE RUBBER INDUSTRY *

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The busy technologist in the rubber industry is continually faced with the problem of choosing, by ready and simple means, the fillers best suited to his needs from the endless number offered him. In many cases there is no information at all about their composition or activity. In examining a filler it is necessary therefore to determine first of all whether it conforms to chemical requirements; whether for instance, it contains any substance poisonous to rubber. The degree of fineness must also be determined. Only if these tests are satisfactory is the filler given its final and conclusive test in a rubber mixing. Obviously there is little time to carry out such a series of tests in a systematic way, so in most cases a standard mixing is chosen to serve as a means of judging a filler.

It is however well recognized that it is very difficult to reach any satisfactory conclusion by such a procedure, since only relative values are obtained, *i.e.*, the values must be compared with those obtained with other fillers. Furthermore in such a test it is almost impossible to maintain the experimental conditions as constant as is necessary when it is intended to compare the results of two series of measurements with one another. It is readily understandable therefore that for a long time rubber technologists have wished for some kind of method which would make it possible to measure in absolute terms the activity of a filler in rubber.

According to the view commonly held today[1], there are two factors which govern the activity of a rubber filler, *viz.*, its particle size and its susceptibility to wetting. Attempts have been made in the past to measure these two properties independently. Thus, some years ago von Hahn and Hahn[2] developed their flocculation meter for determining particle size; others have attempted to utilize adsorption of dyes as a means of comparison. But however much these developments may be of value in other respects or from a scientific point of view, they have been of no value to the rubber industry in analyzing fillers, for the simple reason that in no case do they measure more than one of the two properties mentioned above.

The *plastograph*[3] (see Figure 1) on the contrary offers a means of measuring simultaneously the adsorptive power of a powder and the solidity of the plastic mass formed from the powder by adsorption.

For a better understanding of this apparatus, the principles involved in making the measurements will be described briefly. Figure 2 shows in a simple way the construction.

A small kneader (1) has two horizontal rolls, running in opposite directions, on the surfaces of which are long pins. These pins are so arranged that they comb toward one another and thereby give the material a very thorough mixing.

The kneader is driven by a synchronous motor (2), which is suspended so that it can turn freely (3). Any resistance which is encountered in the powder by the

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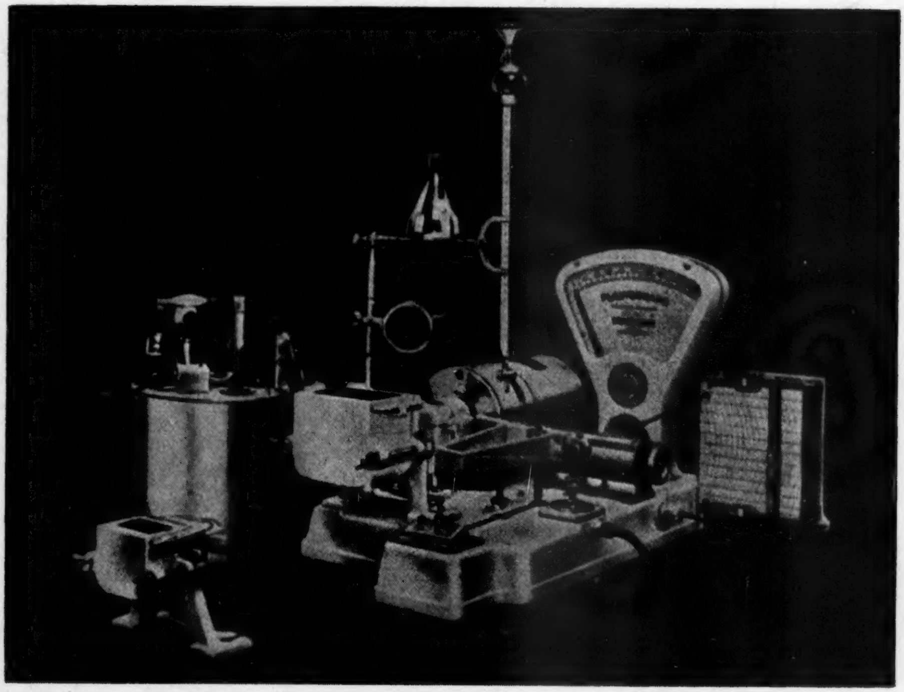

FIG. 1.

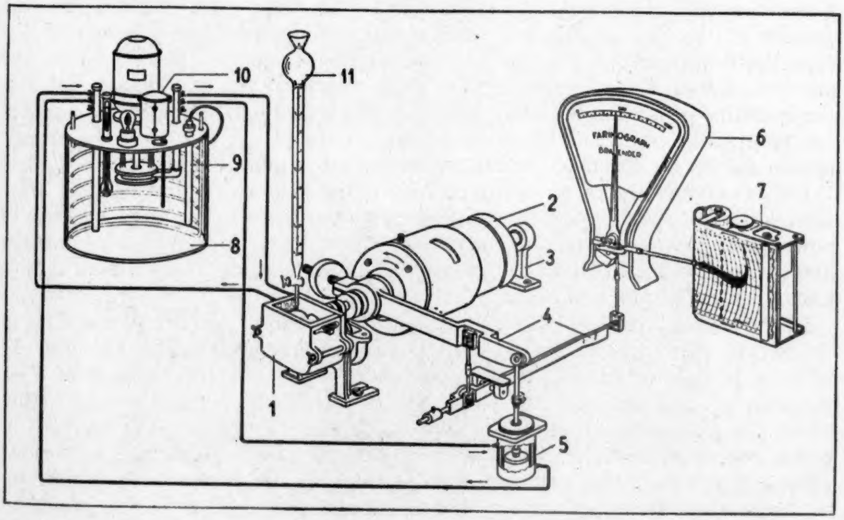

FIG. 2.

pins on the rolls reacts as a force in the casing of the motor which thereby tends to rotate in the opposite direction around the axis. These moments of rotation are transferred by means of a lever (4), the movement of which is dampened by an oil damper (5), to a weighing system (6) and are registered by an electric recording device (7). The chart on which the results are recorded has divisions from 0 to 1000 units (grams) and, by preliminary loading of the weighing system with various weights, this range of measurement can be extended several 1000 units.

The kneader has double walls and therefore can, if desired, be maintained at any constant temperature by means of a circulating thermostat (8).

In experimenting with a filler, the wetting agent is added at a constant rate from a graduated burette, so that the quantity of wetting agent which has been added at any moment in the experiment can be read in cubic centimeters on the time axis of the chart.

Accordingly the conditions in this apparatus are analogous to those in the mixing of rubber with fillers in closed mixers. The only difference lies in the fact that, in the new apparatus, the wetting agent is added to the filler, whereas in a closed mixer the powder is added gradually to the dispersion medium, *i.e.*, to the rubber.

It was evident from the beginning that the development of a satisfactory method for measuring the activity of fillers depends greatly on the proper choice of dispersing agent, provided that any conclusions are to be drawn as to the behavior of the fillers in rubber. In the first series of experiments a 1 per cent solution of Igepon was used as the wetting agent, with whiting, zinc oxide (Red Seal and "active"), lamp black (Elastic) and gas black (Luv 36, P 1250 and Arrow) as fillers. In this series the activity of the fillers in rubber increased in the order given, *i.e.*, whiting was the least active filler, Arrow gas black the most active.

In testing the various fillers, the procedure was in each case to introduce 100 cc. of dry filler into the kneader and then to start the apparatus. As soon as the kneader was in motion, a 1 per cent solution of Igepon was titrated into the powder at the rate of approximately 4 cc. per minute. The progress of the experiment was recorded by the electric graphical registering mechanism, the abscissa of the chart representing the elapsed time of the experiment and also the quantity of wetting agent added, and the ordinate representing the power consumption in grams and hence the solidity of the plastic mixture. The experimental results for the fillers mentioned above are reproduced in Figures 3 to 9.

Let us examine first of all the graph for whiting (Figure 3). Immediately after the addition of the first few cc. of Igepon solution, there was a rapid increase in power consumption, in fact to about 300 grams, then the power consumption fluctuated, next increased to 850 grams, and after reaching its maximum diminished very rapidly to zero reading.

In the case of Arrow gas black (see Figure 4), which is the most active filler in the series, there was no increase in power consumption during the first 17 minutes, in spite of the fact that Igepon solution was added at the rate of 4 cc. per minute. This section of the curve may be termed the *starting period,* within which the power consumption is practically zero. Then follows an increase in power consumption in two steps to the 56-minute point, which may be termed *period of ascent*. After this maximum is reached, the power consumption remains constant to approximately the 66-minute point. This is the *period of stability*. From the 67-minute point on, the power consumption diminishes progressively, and the curve descends gradually to the 91-minute point. The

mixture has then become so soft that practically no power is necessary any longer to knead it. This diminution in the power consumption may be designated as the *period of decline.*

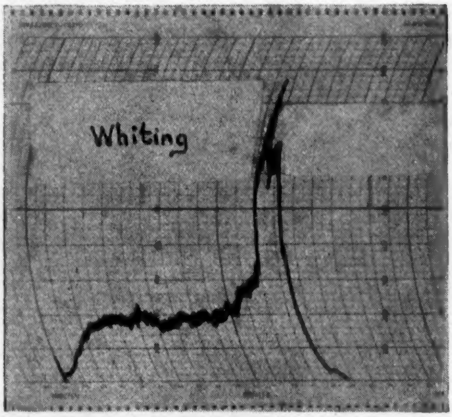

FIG. 3.

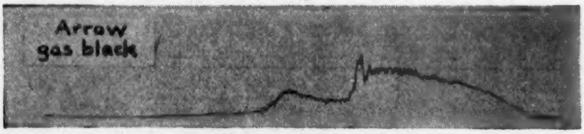

FIG. 4.

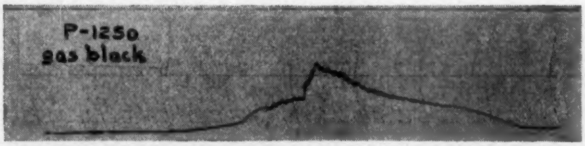

FIG. 5.

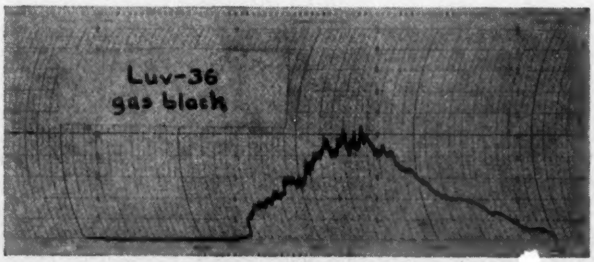

FIG. 6.

The problem then is to explain each of these periods individually. The prolonged starting period of Arrow gas black (see Figure 4) may be explained in the following way. The quantity of Igepon solution which is added during this

starting period is adsorbed by the gas black, without any noteworthy change in the solidity of the mixture. Here a distinction must be made between the internal and outside surface of the particles. Evidently only the internal surface is wetted during the starting period, while the outside surface remains dry. Figure 10 illustrates the structure of the material.

The particles represent the primary particles, which form larger aggregates, the secondary particles. In the interior of the secondary particles there are

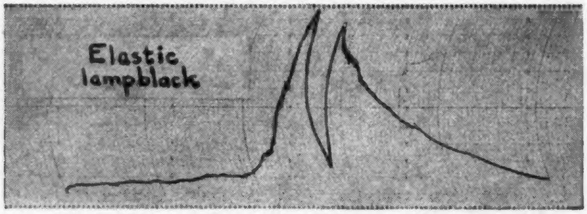

Fig. 7.

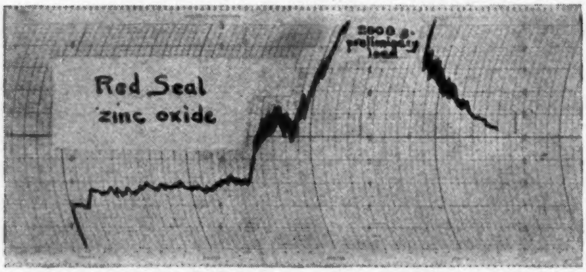

Fig. 8.

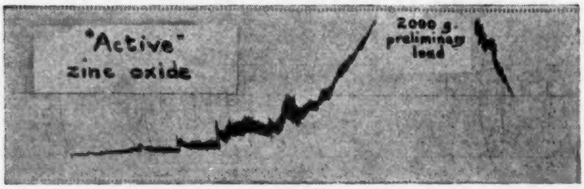

Fig. 9.

naturally empty spaces, which are the first to be wetted, and these spaces may be designated as the internal surface.

During the period of ascent the outside surface too is gradually wetted. As a result, the secondary particles form clusters and at the same time agglomerate, as a result of which the power required to knead the mass increases, since the originally loose structure of the filler is gradually transformed into a crumbly and later plastic mass. As more and more Igepon solution is added, it spreads over the entire surface of the powder until the external surface is completely wetted. At this point the period of stability commences. Further addition of Igepon solution leads to denser packing because of the great affinity of the filler for the wetting agent. On the other hand this additional wetting agent lowers

the viscosity of the mixture at the same time, with the result that a period is reached in which these two effects equalize one another, *i.e.*, the power consumption does not change notably. Only by still greater additions of Igepon solution, whereby the forces of attraction of the gas black particles are saturated, does the entire, hitherto compact mass loosen again. At this point the period of decline begins, with a diminution in the power necessary to knead the mass. The power consumption becomes progressively smaller and finally it reaches a value which depends only on the viscosity of the Igepon solution.

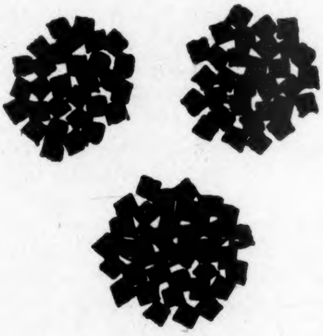

FIG. 10.

On the other hand, in the case of whiting, the particles of which are relatively coarse (see Figure 3), one is led to the conclusion that there is no appreciable internal surface. The Igepon solution wets the outside surface immediately and cements the particles together. For this reason there is no starting period, and the power consumption begins to increase at once. After the power consumption has reached its maximum value, it diminishes immediately, so that there is no period of stability. Evidently the affinity of whiting for Igepon is small, and to this fact may be attributed the rapid decline in power consumption.

Since these experimental results show an unquestionable parallelism with the activity of the powders when functioning as fillers in rubber, it seemed promising to study the behavior of other fillers, the activity of which in rubber are known. Attention was first directed to other blacks. Figure 5 shows the results obtained with gas black P 1250. The data on the various powders tested with Igepon solution are summarized in Table 1.

TABLE I

Filler	Quantity (cc.)	Quantity (grams)	Starting period (min.)	Period of ascent (min.)	Stability period (min.)	Power consumption (grams)	Period of decline (min.)
Whiting	100	280	0	12	0	870	3
Black (Arrow)	100	176	17	39	10	640	25
Black (P 1250)	100	176	17	27	0	600	37
Black (Luv 36)	100	180	14	8	4	500	14
Black (Elastic)	100	180	0	26	0	835	31
Zinc oxide (Red Seal)	100	560	0	22	7	3000	not measured
Zinc oxide (active)	100	560	0	36	12	3000	not measured

The dispersing agent was 1 per cent Igepon solution, which was added at the rate of 4 cc. per minute.

The chart reproduced in Figure 5 is another case where the results correspond to the activity of the filler, for gas black P 1250 is a black which closely resembles Arrow gas black but the degree of activity of which is not quite so great as that of Arrow black.

"Soft" black Luv 36 follows next in order (see Figure 6). Here too the graph indicates a behavior which corresponds to that of the black in rubber.

Elastic Black is next in order (see Figure 7). In this case great fluctuations in the power consumption are evident, so that it is impossible to identify any period of stability. This graph does not correspond at all with practical results obtained with this black in rubber. Probably it is a relatively coarse black, as indicated by the absence of a starting period; however, at the same time its affinity for rubber is less than that of the other blacks. Nevertheless, the graph shows a much greater power consumption and a complete absence of a period of stability.

Finally two types of zinc oxide were investigated, a relatively coarse type (Red Seal, see Figure 8) and an active type of very fine particle size (see Figure 9). Neither graph gives any evidence of a starting period. Furthermore with these fillers too, there seemed to be little relation between their behavior in the kneader and their activity in rubber. Only in the periods of stability does the difference in the two types show a parallelism with their behavior in rubber. Red Seal zinc oxide shows a stability period of 7 minutes, active zinc oxide a stability period of 12 minutes.

As has already been emphasized, much depends in these experiments on the proper choice of dispersing agent. Since, as has been shown, Igepon solution did not in every case reflect the activity of fillers in rubber, it became necessary to search for another more suitable wetting agent. The choice fell on Sangajol, a product which has been used for years in the varnish industry. The chemical composition of Sangajol is similar to that of rubber, and furthermore it can be obtained commercially with uniform properties at all times.

Adsorption experiments were then carried out in the plastograph, with Sangajol as dispersing agent, by the same general procedure as in the first series. One modification was made, however, in that only 75 cc. instead of 100 cc. of powder was used, so that even with very bulky powders the kneader would be large enough to hold the mixture. Thirteen different fillers were studied, all of which are well known in the rubber industry, so that the rubber expert will be able to judge for himself the value of the new method of investigation.

The results of this second series of experiments are shown in Figures 11 to 23, and are summarized in Table 2. In this table are recorded for each filler not only the starting period, period of increase, period of stability, period of decline and power consumption, but also the area under the curves and the sum of the area under the curves and the starting period. The order of the fillers in the table is the order of their activity in rubber.

An analysis of these curves and a comparison of the results with all fillers except zinc oxide and magnesium carbonate leads to the following conclusions.

The more active a filler in rubber, the longer the starting period and the stability period, with however two exceptions. Black Luv 36 showed a shorter stability period than did Elastic Black, whereas Black Luv 36 showed a long starting period and Elastic Black a considerably shorter starting period. An experiment to explain this anomalous behavior will be carried out later. The rapid increases with Luv 36 and Inca blacks are also worthy of note.

On the contrary the behavior of the various types of zinc oxide conformed to expectations. Here too, these are listed in the order of their activity in

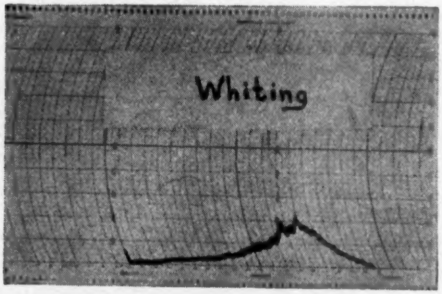

Fig. 11.

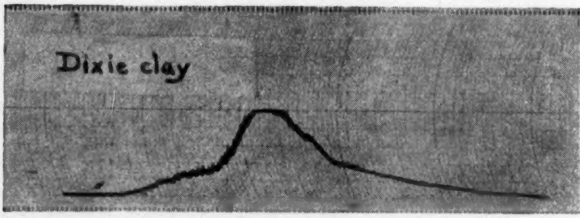

Fig. 12.

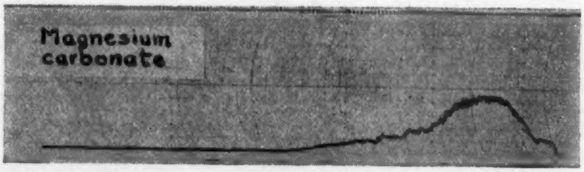

Fig. 13.

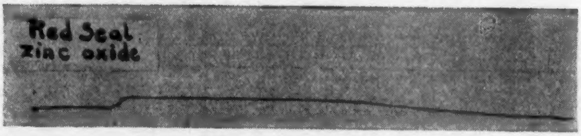

Fig. 14.

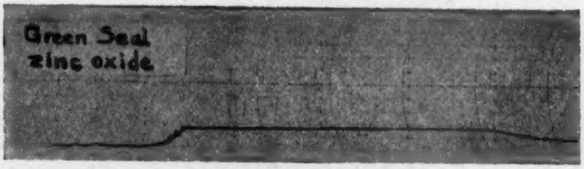

Fig. 15.

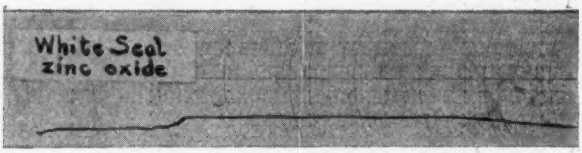

FIG. 16.

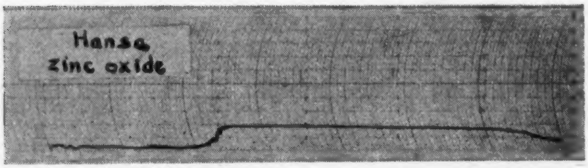

FIG. 17.

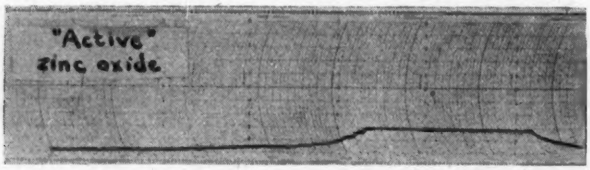

FIG. 18.

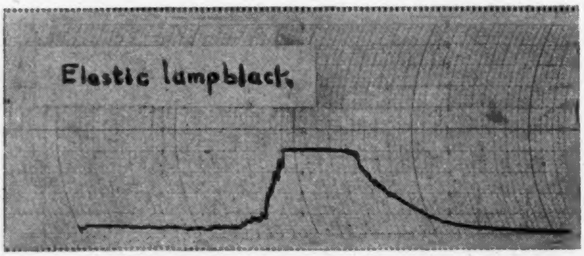

FIG. 19.

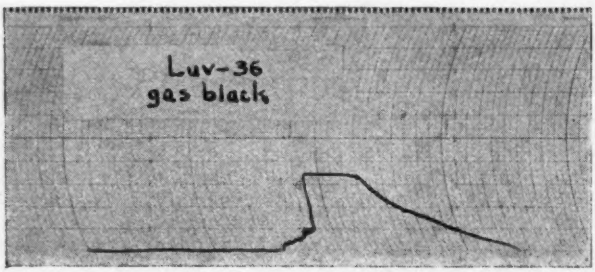

FIG. 20.

rubber. None of the zinc oxides showed any real starting period, but rather a gradual increase in two steps, the longest period of increase being shown by the active zinc oxide. Hansa zinc oxide and White Seal zinc oxide had the same periods of ascent, but the power consumption was less with Hansa zinc oxide. As the least active type, Red Seal zinc oxide had the shortest period of ascent and the highest power consumption during this period.

Finally, the behavior of magnesium carbonate should be noted. This powder showed a very long starting period and period of ascent, a short period of stability and a rapid decline. Furthermore this powder is wetted by Sangajol with great difficulty. It forms a large volume, and the whole mass is not kneaded

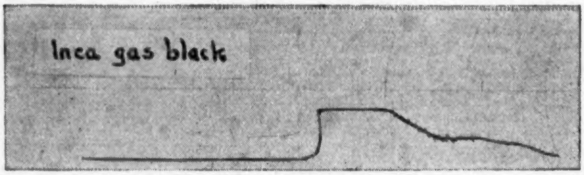

FIG. 21.

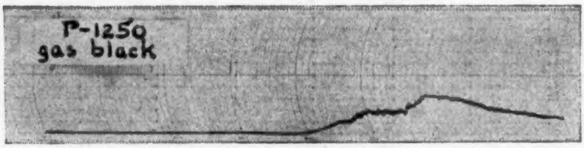

FIG. 22.

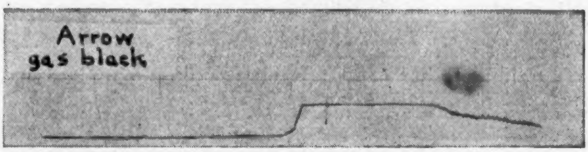

FIG. 23.

uniformly by the combs of the rolls. The curve must not therefore be judged quantitatively. However, it must also be taken into consideration that the mixing of magnesium carbonate into rubber likewise entails great difficulties. It is frequently almost impossible to avoid the formation of aggregates or clumps of powder when the attempt is made to mix this filler alone into rubber, and it is absolutely necessary to use a dispersing agent. Therefore in this case too the method described in the present paper gives at least some information as to the practical utility of this filler. This will be discussed in greater detail in a later paper.

If now the results are considered as a whole; it may be said that, by making a paste of a powder with Sangajol as the dispersing agent, it is possible to obtain a correct idea of the activity of a powdered substance in rubber. In the case of the various types of zinc oxide, the entirely different nature of their activity in rubber is revealed very clearly in the graphs, particularly in the absence of starting periods and in the prolonged periods of stability. These latter are

TABLE II

Filler	Quantity (cc.)	Quantity (grams)	Starting period (min.)	Period of ascent (min.)	Stability period (min.)	Power consumption (grams)	Period of decline (min.)	Surface area (sq. cm.)	Sum of starting period and surface area
Whiting	75	210	1.5	11.5	0	200	4.5	17.6	19.1
Clay (Dixie)	75	187.5	6	16	3.5	500	25.5	123.3	129.3
Magnesium carbonate	75	155	32.5	29	3	450	...	111.9	144.4
Zinc oxide (Red Seal)	75	420	0	16	39	200	45	228.1	228.1
Zinc oxide (Green Seal)	75	420	0	19	43	170	18	153.8	153.8
Zinc oxide (White Seal)	75	420	0	23.5	43.5	180	22.5	207	207
Zinc oxide (Hansa)	75	420	0	24	38	180	18	142.3	142.3
Zinc oxide (active)	75	420	2	42	22.5	190	11.5	115.1	117.1
Black (Elastic)	75	135	0	19	6	400	16.5	92.7	92.7
Black (Luv 36)	75	135	15.5	3.5	4	350	11	55.5	71
Black (Inca)	75	135	28	3.5	9	370	25	117.1	145.1
Black (P 1250)	75	132	38	21	4.5	330	26.5	138.3	176.3
Black (Arrow)	75	132	37	4.5	19.5	300	25	175.3	212.3

The dispersing agent was Sangajol, which was added at the rate of 4 cc. per minute.

longer than the corresponding periods of the active blacks, whereas the power consumption is smaller. The explanation which was offered for the series of experiments with Igepon solution holds true in this case as well. All powders with long starting periods must therefore have relatively great internal surface areas. Hence for a given form of primary particle, the magnitude of this starting period is a relative measure of the particle size of the powder. Unfortunately no precise values of the particle size have yet been obtained, so that it is still impossible to prove the correctness of the views expressed in the present paper. Because of the extraordinary fineness of the powders, especially of the blacks, it is extremely difficult to carry out determinations of particle size. However, an experimental apparatus is being developed, with which it will be possible to carry out such determinations simply and precisely. It will be possible to describe this in more detail in a later work.

In addition to this, the curves give an indication of the magnitude of the external surface area of the secondary particles. The steeper the ascent of the curve, the smaller must be this surface area: in other words, the smaller the number of secondary particles. Since, however, the total volume in each case is the same, these secondary particles must be larger than those of powders with greater external surface areas. The relatively small external surface areas of Inca, Luv 36 and Arrow blacks (see Figures 21, 20 and 23) are particularly striking.

In conclusion something more should be said about the power consumption and the duration of the stability period. It is evident that power consumption is a measure of the affinity of a powder for Sangajol and therefore indirectly of its affinity for rubber. However, the period of stability also must be taken into account in this connection, for it indicates how many cc. of Sangajol can unite with a powder without any change in the solidity of the mixture. Then again in judging a filler, the starting period, period of increase, period of stability and power consumption must be taken into account.

As has already been mentioned, the planimetric surface areas of the diagrams are included in Table 2. These values probably give a good idea of the affinity, but since they are not concerned with the starting periods they give no idea of the size of the primary particles. But the sum of the two values, starting period and surface area, should be a correct measure of the activity of a filler in rubber. Broadly speaking, only the various types of zinc oxide were an exception to this. It has already been seen that this is manifest in the entirely different character of the curves, on which the lengths of the periods of stability are especially noteworthy. An explanation of this is still to be found. Among themselves these fillers fall in an order which corresponds quite well to the order of their activity in rubber.

RÉSUMÉ

A method for measuring the activity of a filler in rubber has been developed, the principle of which involves measuring the adsorption of Sangajol by the filler in a plastograph. Thirteen well known rubber fillers were tested by this method, and it was found that their behavior conformed to the properties which they impart to rubber. The experiments are to be continued, with particular attention to the effect of dispersing agents.

REFERENCES

[1] See, for example, Talalay, "Handbuch der gesamten Kautschuktechnologie", Union Deutsche Verlagsgesellschaft, Berlin, Roth and Co., 1934, p. 217.
[2] von Hahn and Hahn, *Kolloid-Z.* **31**, 352 (1922).
[3] Upon enquiry, the editors will give the name of the manufacturer of this plastograph.

NOTES ON THE METHOD OF ROBERTS FOR THE ANALYSIS OF RAW RUBBER *

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INTRODUCTION

To add to the knowledge of *Hevea* rubber, so that it is possible to profit most by the special properties of this important raw material, it is necessary to isolate and to identify the various components of *Hevea* latex.

A new method to carry this out systematically has been published by Roberts[1].

In this method advantage is taken of differences in solubility in various solvents of the various components of raw rubber.

What struck us most in the paper by Roberts is the statement that the substance in crude rubber which hitherto has been believed to be a hydrocarbon is not a hydrocarbon, but consists of two essential components. One of the components is said to be a hydrocarbon, an octaterpene of the constitution, $C_{80}H_{128}$, to which the name "caoutchene" has been given. The other component, in which oxygen forms part of the molecule, is said to be an alcohol, to which the formula, $C_{80}H_{130}(OH)_2$, is ascribed and which has been named "caoutchol".

According to Roberts, "caoutchene" is to be considered a plastic substance without rigidity and with none of the elastic properties so characteristic of raw rubber.

On the other hand a high degree of elasticity is ascribed to "caoutchol". Roberts holds that the alcohol "caoutchol", as a component of raw rubber, imparts to the latter its elastic properties. The alcohol is also the carrier of the oxygen which is present in raw rubber, be it in small quantities only. Up to the present time the presence of oxygen has been supposed to be the consequence of oxidation of raw rubber by oxygen from the air.

The conception of Roberts is therefore so remarkable that it deviates altogether from current ideas. Considered from a chemical point of view, rubber hydrocarbon must be oxidizable because of its structure. The fact that crude rubber exposed to air exhibits a certain degree of stability is a consequence of the protective action of the by-substances. Once the rubber is dispersed in solvents and thus freed from the protective components, it has become vulnerable, and thus liable to oxidation.

Keeping in mind that Roberts carried out his analysis without certain precautions to exclude oxidation, his statement quoted in a note on page 219 of his paper, which reads:

"The process has been carefully examined, particularly with respect to the possibility of oxidative or other changes in the constituents. No evidence of such changes has been obtained", can only sound strange and lead to a closer investigation of his method.

In the experimental part of this paper it is shown that "caoutchol" is an oxidation product of rubber hydrocarbon.

* Reprinted from the *Archief voor de Rubbercultuur,* Vol. 22, No. 4, pages 231-238, November 5, 1938.

The separation by Roberts of the organic non-hydrocarbon components of rubber and the "precipitated rubber" is founded on the fractional precipitation of the latter from a carbon tetrachloride-acetone mixture (7:4.5), by means of one of the components: acetone (4.5 parts). By following this procedure, Roberts availed himself of the fact that "precipitated rubber" is not soluble in a carbon tetrachloride-acetone mixture (7:9), but that non-hydrocarbons are. Considering that the main component of these non-hydrocarbons, *viz.*, "caoutchol", is completely insoluble in acetone, one must admit that the separation of "caoutchol" and "precipitated rubber" cannot be complete. Nevertheless it will be possible to select the ratio of the solvents: carbon tetrachloride and acetone, in such a way that separation takes place as completely as possible.

We are willing to agree that Roberts has ascertained this ratio, but we wonder whether the amount of "caoutchol" present in the mixture has not also its influence on this ratio 7:9. As it is, Roberts based this ratio on a "caoutchol" content between 2 and 5 per cent. But will this ratio remain unaltered when the "caoutchol" content is 10 or 20 per cent or higher? Most probably not, because in the binary system: carbon tetrachloride-"caoutchol", the solubility of "caoutchene" undoubtedly varies.

We arrived at the above theoretical views because we observed that the higher the "caoutchol" content the more difficult it was to separate non-hydrocarbons and "precipitated rubber" (by decantation, filtration or centrifugation). Moreover we observed that the substance "caoutchol" changed in appearance when more of it had been separated.

That the temperature at which the analyses, according to Roberts, are carried out might influence the results, did not seem out of the question. This would mean that analysis of one and the same sample of rubber carried out in a moderate climate and in a tropical climate would yield different results.

In the experimental part we shall describe an experiment which proves that the results of the analysis depend on the temperature at which it is carried out.

EXPERIMENTAL PART

The procedure followed by Roberts and which was tested by the present authors is shown on page 126.

Investigation into Possible Changes in the Components of Raw Rubber Resulting from Oxidation During the Process of Separation

To investigate this point, the analyses were carried out under different conditions:

For these analyses we used rubber from one sample of pale crepe (No. A-4347). For the experiments, 30 grams of finely divided crepe were weighed for each analysis. This quantity was, according to the prescription of Roberts, dispersed in a mixture of 700 cc. of carbon tetrachloride and 450 cc. of acetone.

Subsequently the following analyses (a-e) were carried out.

Since at present we are above all interested in the occurrence of "caoutchol", we are concerned in this paper only with the left part of the scheme of separation shown above.

The conditions under which the analyses were carried out, are as follows:

With exclusion of oxygen and with solvents which were freed from peroxides.

In a suction flask of 2 liters content fitted with a stopper holding a dropping funnel and a bent glass tube, 30 grams of finely divided pale crepe were put.

Rubber

(Crepe, sheet, evaporated latex, etc.)

disperse in carbon tetrachloride-acetone (7:4.5)
then add acetone (4.5)

- solution (non-hydrocarbon substances: evaporate to dryness on water-bath and extract with water)
  - solution: evaporate to dryness on water-bath = water extract L_1
  - residue: extract with boiling acetone
    - residue: "caoutchol" L_2
    - solution: evaporate to dryness on water-bath and extract with ligroin = total acetone extract
      - solution: evaporate to dryness on water-bath L_3
      - residue: L_4
- precipitate ("precipitated rubber")
  - sediment R_1
  - solution: emulsify in water and distill with steam
    - residue: decant
      - solid part: "crude caoutchene" R_2
      - liquid part: evaporate to dryness R_3
    - distillate

Through the bent tube, nitrogen previously dried and freed from oxygen was led into the flask. As soon as the gas space above the crepe had been freed from air, the mixture of carbon tetrachloride and acetone, previously freed from peroxides, was run into the flask. After sealing the flask carefully it was shaken from time to time. The flask was kept in darkness for 24 hours, the dispersion being under nitrogen all that time. Then by means of the dropping funnel the prescribed quantity of acetone, free of peroxides, was added. The resulting extra pressure in the flask brought about by nitrogen was released by the escape of nitrogen through the dropping funnel. On having stood for another 24 hours the manipulations were carried out open to the air. Oxidation which might occur from this point on would no longer have any influence on the "caoutchol" content.

Under "normal" conditions.

This means entirely according to the procedure of Roberts.

Under somewhat modified conditions.

The dispersion of rubber was purposely stirred excessively with a glass rod, so that air was beaten into the dispersion.

By bubbling a current of air through the dispersion.

The gases of carbon tetrachloride and acetone carried along with the current of air, which was led in during 3.5 hours, were condensed in a flask chilled with ice, which was fitted with a condenser. The condensed vapor was later redeposited in the original dispersion.

By bubbling a current of oxygen from a cylinder through the dispersion of rubber.

Oxygen from a cylinder was bubbled through a dispersion of rubber for 4 hours. Here too care was taken that no loss of solvent by evaporation took place. The results of the analyses are summarized in Table I.

TABLE I

ANALYSES UNDER DIFFERENT CIRCUMSTANCES ON PALE CREPE No. A 4347

Analyses / Components (in per cent)	Water extract (L_1)	Total acetone extract (L_3+L_4)	"caoutchol" (L_2)
a. Under nitrogen	0.17	2.49	0.90
b. "Normal," according to Roberts	0.14	2.57	1.98
c. With beating in of air	0.17	2.42	2.22
d. Air oxidation	0.16	2.35	3.97
e. Oxygen oxidation	0.02	2.20	11.9

From Table I we see that the figures for the water and acetone extracts obtained from the analyses carried out under different conditions are of the same order of magnitude (with exception of the water extract of analysis *e*, carried out in an oxygenous atmosphere, which gives a very low result). In contradistinction to these concordant figures, the figures for "caoutchol" show very considerable differences.

The results of these analyses lead to the conclusion that during the procedure of analysis described by Roberts oxidation occurs.

By operating in a non-oxidizing medium, the "caoutchol" content can be reduced to less than one-half.

The results of the analyses also give rise to the supposition that "caoutchol" is an oxidation product of "caoutchene", a supposition which was proved by the following experiment.

The "precipitated rubber" (this is a product freed from "caoutchol", see schematic outline already shown) obtained according to analysis *b* is milled to a thin sheet, dried and finely divided. From this product, which has the appearance of purified crepe, 30 grams are dispersed in the usual manner in 700 cc. of carbon tetrachloride and 450 cc. of acetone. Through this dispersion oxygen is bubbled for 1.5 hour. On precipitation with 450 cc. of acetone, it is possible, following the procedure outlined, to isolate 27.1 per cent of "caoutchol"[2] (water extract 0.00%; acetone extract 0.82%).

From this experiment it follows that "caoutchol" can be made from "caoutchene" in any desired quantity.

When one follows the directions given by Roberts with exactitude, oxidative changes take place in the components of the raw rubber.

In this connection the following observation may be mentioned.

When evaporating the carbon tetrachloride-acetone mixture, which is necessary to separate the non-hydrocarbons, we observed a distinct odor like menthol when the solution had attained a small volume (15 cc.), which decreased more

and more as evaporation of the liquid on the water bath proceeded, and which finally disappeared.

This odor was also observed when working with the oxidation product of "crude caoutchene."

Influence of Temperature on the Results of the Analysis

This influence was checked by the following simple experiment.

The analysis was carried out in an atmosphere of nitrogen, *i.e.*, dispersion of the rubber and precipitation of the components (outlined in the right part of the scheme) were carried out in a refrigerator at a temperature of 8 to 10° C.

With a sample of crepe No. A-4347, this analysis gave the following results:

	Per cent
Water extract	0.09
Total acetone extract	2.23
"Caoutchol"	0.48

From this analysis it follows that the temperature at which the analysis is carried out influences the results of the analysis, because a difference in temperature of about 20° C[3] brings about a change in the "caoutchol" content of about 45 per cent.

Consequently there must be a difference in the results of analyses carried out in Europe and those carried out in the tropics.

Further we may mention that with each of our analyses we observed that the mixture of carbon tetrachloride and acetone which contains the non-hydrocarbons in solution is more or less, but definitely, cloudy, even when the liquid is filtered instead of decanted as Roberts prescribes. Moreover it is noteworthy that this cloudiness disappears completely when the liquid is warmed a little (to about 40° C). Connecting this observation with the one already mentioned, we may say that relatively slight differences in temperature influence the solubility of "caoutchol" and "precipitated rubber". Theoretically it is necessary therefore to determine another mixing ratio of carbon tetrachloride and acetone for each temperature.

"Caoutchol" as an Oxidation Product of Rubber Hydrocarbon

In the section entitled "Investigation into the possible changes in the components of raw rubber resulting from oxidation during the process of separation", Roberts is followed without taking special precautions, oxidation occurs.

In accordance with the concept that softened rubber[4], and also rubber plasticized at 50° C on a mixing mill, take up oxygen, it was found that there is more caoutchol than normal in samples[5] of *these kinds*. The analyses were carried out in an atmosphere of nitrogen and with solvents free from peroxides.

Table II gives the results.

DISCUSSION

From the experiments described above it is evident that, when following the method of Roberts without special precautions, oxidation takes place.

We should like to consider the "caoutchol" isolated by Roberts as a complex of oxidation products of rubber hydrocarbon.

Now we were impressed by the fact that when the method of Roberts is applied to crepe, taking special precautions to prevent oxidation, a "caoutchol" content will still be observed, although a low one.

TABLE II

ANALYSES OF CREPE, PLASTICIZED RUBBER AND SOFTENED RUBBER; OXIDATION EXCLUDED

Kind of crude rubber / Components (in per cent)	Water extract (L_4)	Total acetone extract (L_3+L_4)	"Caoutchol" (L_3)
Crepe no. A-4347	0.17	2.49	0.90
Crepe no. A-4347 plasticized at 50° C for hr	0.21	2.42	5.44
Ditto for 1 hr	0.33	2.36	10.2
Ditto for 2 hr	0.03	2.30	26.0
Softened rubber no. A-3486-b	0.07	2.01	3.47

This observation leads us to believe that the method of Roberts, applied under conditions which exclude oxidation, would be suitable for detecting oxidation products[6]. For a quantitative determination of these products, one has to consider the arguments on page 125.

We intend to make a further study of the oxidation products in raw rubber.

To begin with, it would be necessary to determine whether latex, as it flows from the tree, contains oxidation products. For this investigation it is necessary to dry the latex quickly, excluding the possibility of oxidation. Up to the present time we have found these conditions difficult to realize. The attempts are being continued, however.

Supposing that in latex there are no oxidation products or only slight amounts, it may well be that during the preparation of rubber, oxidation is considerable or slight, depending on the method used, and the degree of this oxidation controls the content of oxidation products (compare Table II).

CONCLUSIONS

1. When using the method of Roberts, it is necessary to work in an atmosphere of nitrogen and with solvents free of peroxides, at least in the first phase of separation.
2. The product isolated by Roberts, which has been named by him "caoutchol", is an oxidation product of rubber hydrocarbon.
3. The "modified" method of Roberts, *i.e.*, working under nitrogen, must not be used as a quantitative method when there is a great variation in the "caoutchol" content of the rubber.
4. The results depend on the temperature at which the analysis is carried out.
5. When used with exclusion of oxidation, the method of Roberts may prove to be a means of detecting oxidation products in raw rubber.

REFERENCES

[1] Roberts, *J. Chem. Soc.* **1938**, 215.
[2] This experiment also shows that the by-substances of rubber, although they are in dispersion, have a certain amount of protection all the same. In the present case we are dealing with rubber hydrocarbon free of by-substances; oxidation evidently goes very far.
[3] The other analyses mentioned in this paper were carried out at the ordinary room temperature in the tropics of 28-30° C.
[4] Prepared in Java according to the method of Ungar and Schidrowitz.
[5] The plasticized rubber was prepared from the sample of crepe (No. A-4347), with which the analyses mentioned in Table I were carried out.
[6] It will be important to apply a direct oxygen determination, according to Ter Meulen.

THE SPECIFIC GRAVITY OF RUBBER IN HEVEA LATEX *

O. de Vries

Since my former communication on this subject[1] several papers have appeared which form valuable contributions to the interesting problem of the actual specific gravity of the rubber particles in (original or preserved) *Hevea* latex.

Rhodes[2] recalculated his data, and came to an average figure of 0.9064 for the specific gravity of rubber in ammoniated latex, preserved during several weeks in the East, the rubber content being determined after coagulation by acetic acid in the usual way. Using the term proposed in my former paper, this may be called the specific gravity of "crepe rubber in preserved latex", which may differ from that of "crepe rubber in original latex" by the effect of possible changes by the prolonged action of ammonia, by the settling out of the sludge (ammonium magnesium phosphate, mixed with protein-like substances), and other changes that occur in preserved latex. Leaving these unknown factors out of consideration, we have to take into account the fact that the rubber content was determined by acid coagulation, which means that a certain amount of serum substances, principally proteins, was precipitated with the rubber, and may have influenced its specific gravity. In my former communication I have shown that the specific gravity of "crepe rubber in latex" is found lower, the higher the rubber content of the original latex, *i.e.*, the smaller the ratio of serum to rubber, and the smaller, therefore, the amount of acid-precipitated serum proteins in per cent of the rubber. Plotting, in this line of thought, Rhodes' figure in the graph (Figure 1), it will be seen that it corresponds to 45 grams rubber per 100 cc., or about 46.6 in percentage of weight, not abnormal for a preserved latex. Protein, precipitated with the rubber, has a still smaller effect in another figure given by Rhodes, namely, the specific gravity of rubber from a centrifuged cream of 56.7 per cent rubber content (acid coagulation). The corrected figure for the specific gravity of this rubber is given by Rhodes as 0.9011, which in Figure 1 corresponds to 55.5 grams of rubber per 100 cc., or about 58.5 per cent by weight; this is in reasonable agreement with the real figure of 56.7, taking into account the unavoidable errors of an extrapolation, such as in Figure 1.

A further contribution to this subject was made by Schmidt and Stamberger[3], who freed rubber from commercial preserved latex by electrodeposition and dispersion of the resultant paste in 0.06 per cent ammonia in distilled water, and repeating this process until the aqueous phase was free from non-rubber latex components. They determined the specific gravity of dispersions of different rubber content, and calculated the specific gravity of the rubber phase; but in doing this they made what one might be inclined to call the "usual mistake" by calculating the specific gravity of the components from the percentage by weight, instead of from the percentage by volume. I pointed this out to the authors, but a rectification has not yet been published; my estimation is that Schmidt and Stamberger's figure of 0.905 for the rubber phase should be corrected to 0.907. This is rather high, compared with Rhodes' figure, but this may, at least partly, be explained by the fact that Schmidt and Stamberger's figure holds for 18° C, and Rhodes' for about 30° C. It would be interesting to know

* Reprinted from *The India-Rubber Journal,* Vol. 98, No. 15, pages 422 and 424, October 7, 1939.

what the chemical composition of electro-deposited rubber, and especially its protein content, is, compared with that of rubber from latex cream, so as to correlate the specific gravity figure with the chemical composition of the rubber.

A series of figures for latices of different clones has recently been published by van Gils[4], who centrifuged ammonia-preserved latex, a few weeks old, in the East, after diluting it to about 5 per cent rubber content. By diluting the serum in this way, the amount of serum substances precipitated by the acid when the cream is coagulated for the determination of the rubber content is much reduced, and the value of the real specific gravity of the rubber particles in latex will be approached more closely. But that precipitated serum sub-

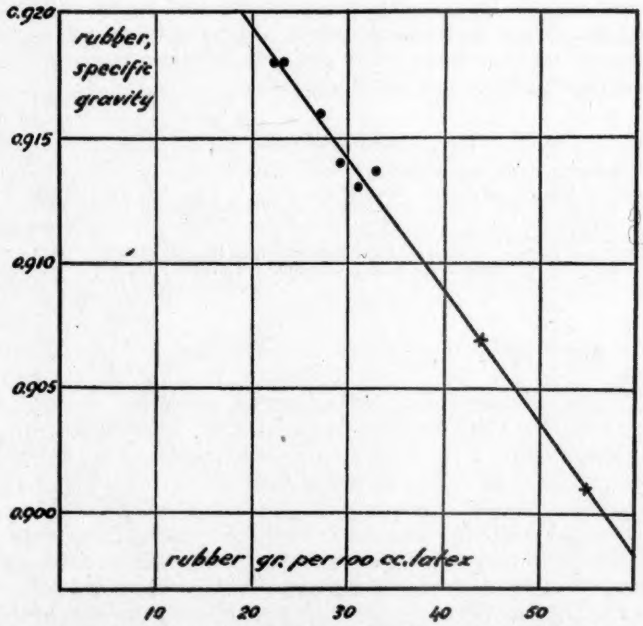

FIG. 1.—Specific gravity of "crepe rubber in latex," for latices of different rubber content. Dots: original latex (de Vries); crosses: preserved latex (Rhodes).

stances still play a role may be seen from the fact that van Gils' figures show a slightly higher specific gravity of the rubber phase for latices with a lower rubber content, the difference being on the average 0.0006 in specific gravity for 10 per cent difference in rubber content (against the much larger figure of 0.0050 in Figure 1).

This makes it probable that the real specific gravity of the rubber phase in the latices investigated by van Gils was lower than 0.904; van Gils mentions that the nitrogen content of the crepes obtained by him was 0.14-0.15 per cent, in good agreement with the figure of 0.13 which we found in former years[5]. We showed that, by diluting the cream with water and repeating the centrifugation, the nitrogen content of this crepe, from washed cream may decrease slightly (to 0.12 per cent), and this will be accompanied by a decrease in specific gravity.

It will be seen that van Gils' figure of 0.904 for acid-coagulated rubber from cream with diluted serum—contrary to what one would have expected—is

higher than Rhodes' figure of 0.901 for acid-coagulated rubber from cream with normal serum. Both figures are subject to the criticism that—besides the influence of acid precipitated serum substances—they may differ from the real specific gravity of rubber in original *Hevea* latex by the changes that take place during preservation, such as precipitation of a sludge (whether the magnesium phosphate is dissolved in the serum, or forms part of a complex protein substance, either in the serum or in the rubber particle, is not yet known, and the changes caused by the addition of ammonia, of which the chemical nature is still unknown, but which are clearly shown by that very sensible method, the determination of rate of cure in a rubber-sulfur mix and of viscosity in 1 per cent benzene of the rubber, by which method[6] changes in the by-substances, as well directly after addition of the ammonia as in the first weeks of keeping, come clearly to light. These and similar points will have to be solved by further investigations if one wants to know the true specific gravity of the rubber particles, as they occur in original *Hevea* latex.

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THE ACTION OF PYRIDINE ON CHLORINATED RUBBER *

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INTRODUCTION

In the various publications on the properties of chlorinated rubber which have appeared, the solubility in pyridine has been mentioned frequently. In 1935 and 1936 the present authors had occasion to occupy themselves with this problem, and the present paper deals with some of the results which were obtained.

Chlorinated rubber is extremely soluble in pyridine, even in the cold; in fact from a practical point of view the solubility is unlimited, and chlorinated rubber and pyridine may almost be regarded as miscible in all proportions. Two definite phenomena were observed during the dissolution of chlorinated rubber on pyridine: (1) a gelation of the system, and (2) the formation of a quaternary pyridinium salt. By the correct choice of conditions, the reaction can be made go, at least partially, to either of these two directions.

GELATIN

Gelation may take place either in a third solvent or by the direct action of the two components on one another.

In the Presence of a Third Solvent.—Two grams of chlorinated rubber[1] were heated with a solution of 3.014 grams of pyridine (this quantity corresponded to 1 mol of pyridine per atom of chlorine) in 20 cc. of anhydrous xylene. After heating on a water-bath for several hours, gelation was complete. The solvent was then distilled away under reduced pressure, and the residual mass was crushed, dried in an oven and pulverized. The product was a black-brown powder, insoluble in all ordinary solvents. After it was washed repeatedly with acetone, a determination by the Carius method gave a chlorine content of 43.8 per cent. Nitrogen was absent.

Other investigators have found that similar gelation can be brought about by means of organic bases[2] having basicities greater than pH=9. In this earlier work, the action of these bases on chlorinated rubber was compared with the vulcanization of rubber, and attention was called to the possibility of using the resulting products for insulating electric cables, etc. Incidentally pyridine was not mentioned.

Nielsen[3], who has discussed this patent and who was probably not aware of the great difference in chlorine content between the original chlorinated rubber and the products formed by the action of bases, attributed the phenomenon merely to a change in size of the macromolecules.

Contrary to this, the results described above seem to the present authors to indicate that, at least to an approximate degree, the insolubility of the product after treatment by a base is a function of its impoverishment in chlorine with respect to the original product.

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In the present work also the action of gaseous ammonia on chlorinated rubber in xylene at water-bath temperature was studied. Although the product obtained by this treatment still contained 51.0 per cent of chlorine, its physical properties were similar to those of the product obtained by the action of pyridine.

Direct Action of the Two Components.—By heating a solution of chlorinated rubber in pyridine on a water bath, gelation takes place rapidly, irrespective of the proportions of the two components. When the solution is cold, gelation takes place much more slowly. Also the higher the concentration of the chlorinated rubber, the faster is the rate of formation of the gel.

The gels obtained in this way are similar to the gels obtained in xylene. With sufficiently dilute solutions, a quaternary pyridinium salt is formed in visible quantities, and this appears before there is any visible gelation.

FORMATION OF A QUATERNARY PYRIDINIUM SALT

Two solutions of different concentrations (1 and 5 per cent) of chlorinated rubber in pyridine were prepared. These solutions were allowed to stand undisturbed for several years, except that aliquot samples were removed from time to time. Only the percentage of ionized chlorine in each of these samples was determined. In these analyses the pyridine solution was poured into water, with vigorous agitation, the aqueous solution was filtered, the filtrate was acidified by nitric acid and was treated with silver nitrate according to the classic method. The following results were obtained.

(1) Five per cent solution (4.9618 grams of chlorinated rubber in 100 cc. of solution).

Time of storage in days	Loss of chlorine as percentage of the total chlorine
10	3.3
25	5.2
35	6.0
45	7.3
60	9.0
85	10.0

After 90 days, gelation had taken place and no further analyses could be made, for the gel could not be disaggregated in water.

(2) One per cent solution (1.0024 gram of chlorinated rubber in 100 cc. of solution).

Time of storage in days	Loss of chlorine as percentage of the total-chlorine
10	6.4
25	10.4
35	10.9
45	11.3
85	12.8
109	16.5
133	17.1
158	19.8
214	23.2
315	26.1
490	35.6

The product was allowed to stand for a long time and was examined again only after 1100 days. It had been partially gelled.

It might at first thought be supposed that pyridine acts as a simple agent of dechlorohydration of the chlorinated rubber, as was suggested in connection with the formation of gels.

In this case, all of the ionized chlorine which was found and determined should be in the form of pyridine hydrochloride. But it can be demonstrated that this is not so; in fact by diluting the pyridine solution strongly with water, filtering, evaporating on a water bath, adding water to the residue, evaporating again and repeating this dilution and evaporation several times to remove all free pyridine, there is obtained a brown solid containing the chlorine in ionized form, which does not liberate any pyridine by the action of sodium hydroxide.

On the contrary, brownish basic substances, with an odor very characteristic of *N*-alkyl-α-hydroxydihydropyridines or their transformation products, are obtained, and these are strictly analogous to those formed by decomposition of quaternary ammonium salts, derived from pyridine, by the action of sodium hydroxide.

The reaction is also remarkably similar to that between pyridine and one of the simplest of the polyhalogenated hydrocarbons, *viz.;* 1,2-dibromoethane, which was carried out under comparable conditions. Even when cold, 1,2-dibromoethane and pyridine form the quaternary pyridinium salt, which reacts with sodium hydroxide as do the bases with the odor of *N*-alkalyl-α-hydroxydihydropyridines. This is also true of other analogous dihalogenated hydrocarbons, but further discussion of this subject is withheld until later.

The similarity between the two reactions is therefore very close, and one is led to the conclusion that the product formed by the action of pyridine on chlorinated rubber is probably a macromolecular quaternary pyridinium salt.

As a matter of fact the existence of heteropolar molecular colloids is not new, for sodium salts of polyacrylic acids, quaternary ammonium salts of polyamines and even polyammonium polyacrylates have been known for a long time. Then again rubber dibromide itself and triethylphosphine form rubber phosphonium bromides, although they are more difficult to prepare than the other compounds and their constitutions are known less precisely[4].

Like all macromolecular products, the ammonium salts and particularly the phosphonium salts, are mixtures of polycondensed products, with molecules of various lengths and can, by dialysis, be separated into fractions of widely differing viscosities.

In conclusion then, the dissolution of chlorinated rubber in pyridine does not appear to be a simple physical phenomenon. In addition to the phenomenon of physical dissolution, there is certainly a chemical reaction, involving the formation of a rubber pyridinium chloride. This can be observed by carrying out the reaction in the cold and at very low concentration, under which conditions the formation is very slow. Gelation, with formation of a strongly dechlorohydrated chlorinated rubber, takes place when the reaction is carried out hot and at relatively high concentration.

Since it is impossible at the present time to continue the investigation described in the present paper, the authors have decided to publish these preliminary experiments and to point out the interesting features.

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TENTATIVE PROCEDURES FOR TESTING THE VARIABILITY OF NORMAL AND CONCENTRATED LATEX *

CRUDE RUBBER COMMITTEE, DIVISION OF RUBBER CHEMISTRY, AMERICAN CHEMICAL SOCIETY

R. H. GERKE, CHAIRMAN, U. S. RUBBER COMPANY, PASSAIC, N. J.

The Committee desires to emphasize that these tentative procedures for testing variability are not to be considered as actual specifications for buying or selling latex, since tolerances or limits are not given. Rather, it is the desire of the Committee to give what are believed to be reliable methods for the determination of the various properties of latex which have been listed. However, it may be necessary to revise some of these procedures from time to time, since the use of latex is in its infancy and improved methods are being rapidly developed. In listing these procedures the Committee does not mean to suggest that it is always necessary to use all of them in testing a sample of latex. In other words, it is up to the users and suppliers to select such methods and tolerances as they see fit which will best suit their purposes.

The Committee desires to express deep appreciation to those who have been instrumental in preparing the attached procedures:

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SAMPLING LATEX *

1. Latex in Drums, L-1a.—*Outline.*—The contents of the drum are thoroughly mixed and the sample is removed by means of a sample bottle.

Details.—In case the sampling operation takes place immediately after the drum is filled, no further mixing is required. In case the drum has stood, the top should be removed and the contents stirred with a high-speed stirrer for 10 minutes.

Attach a 1-liter (32-ounce) open bottle to a 120-cm. (4-foot) length of 0.625-cm. (0.25-inch) steel rod. Introduce the bottle thus attached to the rod into the drum and run it down through the entire body of latex. Withdraw the bottle, discard the contents, refill the bottle and stopper tightly. This double filling eliminates the possibility of diluting the sample with water which may be present initially in the bottle. It will be found advantageous to leave a small air space in the top of the bottle after the second filling in order to facilitate mixing before weighing out samples.

If closed-head drums are used, a procedure of rolling and up ending the drums must be resorted to. Rolling alone is not sufficient. If there is a free air space in the drum, satisfactory mixing can be accomplished within a short time by this means. In case of full drums, transfer all the latex in the closed-head drum to a larger vessel and then take sample according to either of the above procedures.

2. Latex in Tank Cars, L-1b.—*Outline.*—The contents of the car are thoroughly mixed and a sample is obtained by introducing a 1-liter (1-quart) sample bottle attached to a 300-cm. (10-foot) length of 0.625-cm. (0.25-inch) steel rod.

Details.—In case the tank car has been freshly filled, no further mixing will be necessary. If the car has stood, it will be necessary to mix the latex by means of a jet of air from a 1.25-cm. (0.5-inch) pipe inserted through the dome cover of the car and moved continuously throughout the body of the latex. In the case of normal latex, this operation should be continued for 15 minutes, and in the case of creamed or centrifuged latex it should be continued for about 45 minutes.

When the contents of the car have been thoroughly mixed, introduce a 1-liter (32-ounce) narrow-mouthed sample bottle attached to a 300-cm. (10-foot) length of steel rod. Withdraw the bottle and empty the contents back into the car. This initial filling minimizes the possibility of errors from moisture which may be in the bottle. Next, force the bottle quickly down through the body of the latex and raise and lower it rapidly through the entire depth of the tank car several times. On account of the narrow mouth, there will be time to do this during the period of filling of the bottle. Withdraw the bottle when it is completely filled. Pour out just enough latex to leave a small air space in the top and stopper tightly.

DETERMINING TOTAL SOLIDS, L-2

Outline.—A weighed sample of latex is dried down for a given length of time under specified conditions of temperature. The film is then weighed and the result of the determination is expressed as percentage of total solids based on the whole original latex.

Details.—Weigh out 2.5 ± 0.5 grams of the latex to be tested into a covered tinned ointment can or small covered dish which has been tared. The latex should be uniformly distributed over the bottom of the dish during drying. The area

* The procedure for sampling latex is given as an example, and may obviously be altered in certain details.

of the latex should be approximately 32 sq. cm. (5 square inches). Remove the cover and dry the sample in air for 16 hours at 70° C. The percentage of total solids may be calculated by means of the following equation:

$$\text{Percentage of total solids} = \frac{100 \times \text{weight of dried film}}{\text{weight of latex sample}}$$

DETERMINING DRY RUBBER CONTENT, L-3

Outline.—A weighed sample of latex is coagulated with acid, then washed and dried at an elevated temperature. The result is expressed as percentage of dry rubber content based on the whole original latex.

Details.—Weigh out into a porcelain evaporating dish a representative sample of not less than 20 grams of normal latex or 10 grams of concentrated latex and add distilled water until the total solids content is approximately 25 per cent. To this add 2.0 per cent acetic acid solution with stirring until the latex appears to be coagulated and more acid produces no effect. Place the dish on a steam bath and leave for 0.5 hour. Pour off the serum and replace with distilled water. Remove the coagulum and pass between the tightly closed rolls of a laundry wringer or similar device; then wash again with distilled water and wring out. Repeat this process five times. Dry the resulting crepe to constant weight at 70° C. Calculate the dry rubber content as follows:

$$\text{Dry rubber content} = \frac{\text{weight of dry coagulum} \times 100}{\text{weight of sample}}$$

DETERMINING COAGULUM, L-4

Outline.—A weighed sample of latex is filtered and the coagulum remaining on the filter is washed and dried. The result is expressed as percentage of coagulum based on total solids.

Details.—A steel pipe union of about 3.75 cm. (1.5-inch) inside diameter is fitted with a one-hole stopper into a suction flask. Between the two parts of the union, a tared circular section of 80-mesh stainless steel screen is inserted so that when the union is screwed together this screen is held firmly in place.

In order to determine coagulum, weigh out 200 grams of latex from a well-stirred sample and dilute with an equal volume of 5 per cent alkali soft soap solution. Sodium or potassium oleates are recommended. Filter this mixture through the 80-mesh sieve in the steel union and wash the coagulum remaining on the filter with 5 per cent soap solution. Finally wash the coagulum free of soap with distilled water. Remove the screen from the union and dry to constant weight at 70° C. The difference in weight of the screen and the weight of the screen plus coagulum held back represents the weight of dried coagulum. Calculate the percentage of coagulum as follows:

$$\text{Percentage of coagulum} = \frac{10{,}000 \times \text{weight of dried coagulum}}{\text{weight of latex sample} \times \text{percentage of total solids}}$$

DETERMINING METHYL RED TITER OR ALKALINITY, L-5

1. Latex Containing No Fixed Alkali or Base Other Than Ammonia, L-5a.—*Outline.*—The ammonia in a weighed sample of latex is titrated directly with a standard acid solution, using methyl red as an indicator. The result is expressed as percentage of dry ammonia (NH_3) based on the whole original

latex. (The precision of this method is affected by the presence of phosphates and proteins in the latex, which may lead to apparent ammonia contents as much as 0.05 per cent too high, based on the weight of the sample.)

Details.—Pour approximately 10 cc. of the latex into a tared weighing bottle. Immediately cover the bottle. Weigh it to ± 0.05 gram. Place 300 cc. of distilled water in a 600-cc. beaker. Uncover the weighing bottle and immediately immerse it in the water in the beaker. Stir the solution thoroughly with a glass rod. Add 6 drops of a 0.1 per cent alcoholic solution of methyl red and titrate with approximately 0.1 N standard acid until the indicator becomes pink. The end point occurs before complete coagulation takes place and the color change of the indicator can be detected against the white background of the slightly curdy latex. High results will be obtained if the addition of acid is continued until complete coagulation occurs. The calculation is carried out as follows:

Let w = the weight of the sample of the latex
N = the normality of standard acid
n = the number of cc. of standard acid necessary to neutralize the ammonia

$$\text{Then the percentage of ammonia} = 1.7\,\frac{(N \times n)}{(w)}$$

PRECAUTION.—In a direct titration of latex with acid, the acid should not be added so rapidly as to produce local coagulation. Continuous stirring and a moderate rate of addition of the acid are recommended to avoid this.

2. PROCEDURE FOR TOTAL AMMONIA CONTENT, L-5b.—*Outline.*—The ammonia is distilled from a weighed sample of latex, to which has been added an excess of magnesium oxide, into a measured quantity of standard acid. The excess acid is back-titrated with standard alkali solution.

Details.—Weigh out 10 cc. of latex, dilute with water to about 250 cc., and add 4 grams of magnesium oxide. From this mixture distill about 100 cc. into 0.1 N sulfuric acid, the amount of the latter exceeding by about 10 cc. the amount used for the determination of the alkalinity. Boil the distillate for 2 minutes and after cooling determine the excess of sulfuric acid by titration with 0.1 N alkali, using methyl red as an indicator.

DETERMINING pH IN LATEX, L-6

It is recommended that anyone about to undertake the making of measurements of pH without having had previous experience in the use of electrometric apparatus should consult Clark's book[2] in order to familiarize himself with the general technique.

OUTLINE.—The only suitable means for the accurate determination of pH in latex is the glass electrode.* It may be used in conjunction with any one of the various potentiometric arrangements commercially available. In order to make a measurement of pH, the glass electrode is dipped into the solution under test and suitably connected to the reference half-cell and potentiometer. The potentiometer is then balanced and, by means of equations detailed below, the potentiometer reading is converted to pH units.

DETAILS.—*Description and Use of Glass Electrode.*—There are two types of auxiliary apparatus which may be satisfactorily used with the glass electrode: (1) a standard battery circuit with a student-type potentiometer and a reflecting galvanometer of sufficient sensitivity; (2) a battery circuit with a vacuum-tube

* The reasons for restricting the specification to the use of the glass electrode have been discussed in detail by Jordan, Brass, and Roe[5].

galvanometer. Several instruments of the vacuum-tube type are commercially available, some of which require a separate potentiometer and some of which are completely self-contained. For details of preparation and maintenance of glass electrodes and auxiliary apparatus reference must be made to the pamphlets and circulars describing the various individual types of apparatus.

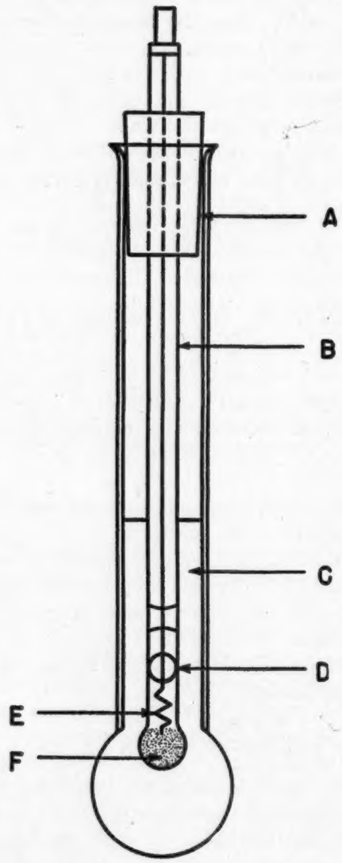

FIG. 1.—Glass electrode assembly.

A. Rubber stopper.
B. Inner electrode.
C. Hydrochloric acid solution at pH 1.
D. Opening for introduction of quinhydrone.
E. Platinum electrode.
F. Quinhydrone.

An essential part of the glass electrode is always a thin shell blown on the end of a glass tube of specific composition. This shell contains a standard reference electrode, usually of quinhydrone in a solution of unit pH. When an individual shell has once been prepared for use, it must be calibrated with the help of standard buffer solutions, the pH of which has been determined by means of the hydrogen electrode. When the electrode has been suitably calibrated (detailed directions are to be found below), it is ready for use.*

In order to measure the pH of an unknown solution, bring the solution to be tested to a temperature of 25° C or to the operating temperature which prevails in the control test. (A water thermostat kept at this temperature should be available. The calomel reference electrode and the potassium chloride bridge solution should be suitably immersed in this thermostat.) Insert the glass electrode in the test solution so that the bulb is completely immersed and make the usual electrical connections, including the introduction of a salt bridge between the test solution and the beaker containing the saturated potassium chloride bridge solution, if a separate calomel electrode is used. Balance the potentiometer with respect to the standard cell in accordance with the directions in Clark's book[4] or in the pamphlets of directions furnished with special forms of apparatus. When this has been done, replace the standard cell by the glass electrode cell and balance the potentiometer against the latter. The potentiometer reading so obtained may be in terms of volts or directly in pH units depending on the type of apparatus employed. If it is obtained in terms of volts, the reading may be converted into pH units by means of the following equation:

$$\text{pH} = A(E - E_0) \tag{1}$$

where E is the observed potential in volts of the glass electrode—calomel electrode cell as read on the potentiometer, and A and E_0 are constants for any given electrode at a constant temperature.

If the reading is directly in terms of pH units, no such conversion is required, but a calibration curve of the individual electrode should always be obtained and the corrections to scale readings should be utilized in testing unknown samples.

The determination of numerical values for these constants constitutes the calibration of any particular electrode and is described in the next section. When these numerical values are known, pH values may be calculated directly from the potentiometer readings by means of Equation 1.

Calibration of Glass Electrode. Prepare two standard buffer solutions as follows:

1. Add 50 ml. of 1 N potassium hydroxide solution to 50 cc. of 2 N acetic acid solution and make up with distilled water to 500 ml.

2. Dissolve 10 grams of anhydrous potassium bicarbonate in water, add 50 cc. of 1 N potassium hydroxide solution, and make up with distilled water to 500 cc.

It is essential to use potassium hydroxide rather than sodium hydroxide in preparing these buffers, since the glass electrode gives incorrect values in solutions containing sodium ions above a pH of 10. Determine the numerical pH values of solutions 1 and 2 by means of the hydrogen gas electrode in accordance with directions in Clark's book[3]. (If sodium hydroxide could be used the hydrogen electrode standardization could be avoided since it is easily possible to obtain carbonate-free sodium hydroxide. However, it is much more difficult to obtain carbonate-free potassium hydroxide, and hence the hydrogen electrode standardization cannot be avoided.) When these buffers have been prepared and standardized, the next step is to find the value of the potential of the glass electrode cell when the glass electrode is immersed in each of the standard buffers. Let

pH_1 = pH of standard buffer solution 1 as determined by the hydrogen electrode
pH_2 = ph of standard buffer solution 2 as determined by the hydrogen electrode
E_1 = glass electrode potential in standard buffer solution 1
E_2 = glass electrode potential in standard buffer solution 2

Then from Equation 1

$$\begin{aligned} pH_1 &= A(E_1 - E_0) \\ pH_2 &= A(E_2 - E_0) \end{aligned} \tag{2}$$

By solution of the simultaneous system (2) for A and E_0, the following results are obtained:

$$A = \frac{pH_1 - pH_2}{E_1 - E_2} \tag{3a}$$

$$E_0 = \frac{pH_1(E_1 - E_2)}{pH_1 - pH_2} \tag{3b}$$

If the standard buffer solutions are protected from atmospheric contamination, they will not change in pH appreciably over a period of several months. Hence,

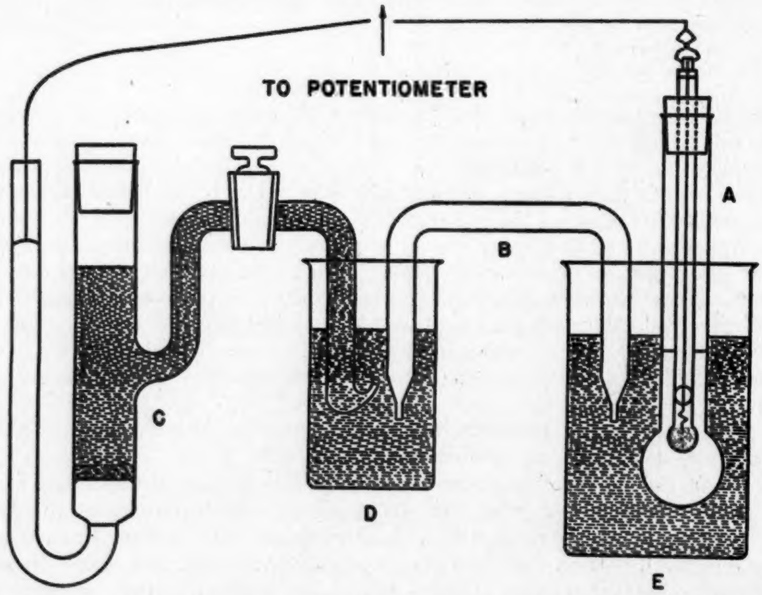

FIG. 2.—Glass electrode-calomel electrode assembly for use with apparatus not completely self-contained.

A. Glass electrode.
B. Agar agar saturated potassium chloride bridge.
C. Saturated calomel electrode.
D. Beaker containing saturated potassium chloride solution.
E. Beaker containing solution under test.

the hydrogen electrode standardization need only be repeated at intervals of, say, one month. However, the calibration of the glass electrode should be repeated at frequent intervals; daily, if the glass electrode is in steady use. The aging characteristics of glass electrode shells vary somewhat from shell to shell, and consequently frequent checking of each individual electrode is absolutely essential.

Precautions. On account of the high electrical resistance of the glass electrode and the susceptibility of vacuum-tube galvanometers to external electromagnetic

disturbances, special precautions are frequently required to shield the glass electrode outfit from such external disturbances.

If a vacuum-tube galvanometer is used, it has been found advisable to place the water thermostat together with the calomel and glass electrode half-cells within a metal jacket which can be completely closed while the potentiometer is being balanced. This metal jacket and the one side of the potentiometer should be grounded, and the electrical connections to the ungrounded side of the potentiometer should be as short as practicable. If an ordinary battery circuit is used in conjunction with the potentiometer, the galvanometer should be protected from stray sources of e. m. f. by grounding one terminal of the galvanometer and shielding it by means of a moisture-proof box. Frequent testing of the glass electrode in the standard buffers will serve as a check on the presence of external disturbances in the electric circuit. A variation of more than 10 millivolts in the glass electrode potential of either of the standard buffers, provided the buffers themselves have not changed (a point which should be checked with the hydrogen electrode) is an indication of difficulties with the electrical system.

The glass electrode fails in solutions of high pH containing sodium ions; hence, it is impossible to determine pH with the glass electrode in latices stabilized with sodium hydroxide.

When the glass electrode is used in latex, it should always be washed free of latex as soon as the determination is finished; otherwise coagulation may take place on the fragile glass membrane. In case a light skin of coagulum does form, it may be removed by rubbing the bulb with a soft wet brush.

DETERMINING VISCOSTIY AND YIELD POINT OF LATICES, L-7

Outline.—Two methods have been found satisfactory for the determination of viscosity and yield point of latex—namely, the capillary flow method and the rotating coni-cylindrical viscometer method. The former is advantageous on account of its simplicity and on account of the fact that the apparatus may be constructed from materials stocked in the laboratory. When the capillary viscometer is made in accordance with dimensions hereinafter specified, it is perfectly adapted to the measurement of viscosities of normal and concentrated latex up to 60 per cent total solids. In general, this instrument has the further advantage that results may be obtained in absolute units from a knowledge of the dimensions of the instrument and without recourse to calibration with a liquid of known viscosity. The rotating cylinder viscometer is rather expensive on account of details of its construction. However, this instrument has a wider range of applicability in dealing with latex than is possessed by the capillary flow apparatus and is in addition, from the theoretical point of view, the most satisfactory method of measuring the viscosities of non-Newtonian liquids like latex. In particular, the rotating cylinder viscometer may be used to measure the viscosities of high-solids latex material like Revertex. A description of this instrument is given by Mooney and Ewart[6]. Specifications will be confined to the capillary flow method.

The capillary flow method consists of measuring the rate of efflux of the liquid to be tested through a capillary tube of known length and known radius under two known pressure heads. The limiting coefficient of viscosity, which is defined explicitly in a later section, is calculated from these data and is expressed in centipoises at 25° C. The yield value is expressed in grams per square centimeter.

Experimental Details.—*Apparatus.*—The apparatus is pictured in Figure 3. It consists of two parts: a glass tube 80 cm. long and 1.2 cm. in inside diameter, and a capillary glass tube 10 cm. long and of known internal radius. Capillary tubes of different radii are specified for differing materials. On the large glass

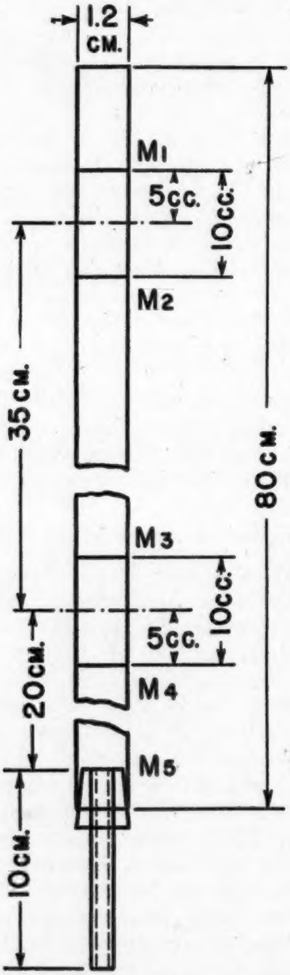

Fig. 3.—Viscosity apparatus.

tube the marks M_1, M_2, M_3, and M_4, as shown in Figure 3, are so placed that the volume included between M_1 and M_2 is 10 ± 0.05 cc. An equal volume is included between M_3 and M_4. The mid-points of the intervals M_1M_2 and M_3M_4 should be separated by a distince of 35 cm. The capillary tube is inserted in the lower end of the 80-cm. cylinder by means of a one-hole stopper. It should be adjusted so that the upper end of the capillary is at a distance of 20 cm. below the mid-point of section M_3M_4 and 55 cm. below the mid-point of section M_1M_2.

Procedure for Determining Viscosity and Yield Point.—Assemble the glass tubes precisely as shown in Figure 3 and as described in the preceding paragraph. Hold one finger over the lower end of the capillary and fill the tube with latex to a point about 5 cm. above M_1. Place a beaker under the lower end of the capillary and allow the latex to run out through the capillary. By means of a stopwatch, determine to the nearest tenth of a second the time required for the meniscus to pass through the interval in the 80-cm. tube bounded by marks M_1 and M_2. Similarly determine the time occupied by the meniscus in passing from M_3 to M_4. If difficulty is experienced in seeing the meniscus, a small flash light placed behind the tube will be found helpful. Measure the temperature of the latex to the nearest 0.5° C just prior to conducting the viscosity determination. During the passage of the meniscus from M_3 to M_4, efflux from the capillary may take place dropwise. This is undesirable and can be prevented by bringing the lower end of the capillary nearly into contact with the latex in the receiving beaker.

Calibration of Capillary. Clean the capillary with chromic acid solution, wash with distilled water and finally dry; then clamp the capillary in a nearly horizontal position and slowly pipet clean mercury into the upper end until it just flows out at the lower end. Scrape off the protruding meniscus by means of a spatula which is then held tightly against the capillary, and withdraw the pipet so that the capillary is completely filled with mercury. Likewise scrape off the meniscus protruding from the upper end. Empty the mercury contained in the capillary into a weighing bottle and weigh. Duplicate determinations should agree to 0.1 per cent. Determine the length of the capillary by means of a caliper or traveling microscope to the nearest 0.1 cm. Then, if

R = radius of capillary in centimeters
L = length of capillary in centimeters
W = weight of mercury contained when the capillary is full
D = density of mercury at temperature of measurement

the equation giving the radius is

$$R=\sqrt{\frac{W}{\pi LD}}$$

It is of great importance that the capillary be of uniform bore throughout its length. This can be checked up as follows with the aid of a microscope with a traveling stage. Place enough mercury in the clean capillary to fill it about half full. Measure the length of the mercury column in a random position in the tube by means of the microscope. Then tilt the tube so as to shift the position of the column of mercury to another section of the tube, taking care not to lose any mercury, and again measure its length. Repeat this several times. The length of the thread of mercury should not vary from place to place by more than 0.1 per cent.

Preparation of Latex for Viscosity Measurement. All viscosity measurements on concentrated latices should be made at 60 per cent total solids and on normal latices at 35 per cent total solids. After the adjustment of the total solids content, prepare the latex for a viscosity measurement by straining it through a 200-mesh silk sieve and deaerating it overnight. In case partial creaming takes place during the deaeration process, gently swirl the container while the latex is under reduced pressure to stir in this cream. Care should be taken that no bubbles are formed.

TYPES OF CAPILLARY FOR USE WITH NORMAL AND CONCENTRATED LATICES

Type of latex	Radius of capillary cm.
Normal	0.040 ± 0.002
Concentrated, 60%	0.070 ± 0.004

Calculations.—In terms of Figure 3, let

t_1 and t_2 = times in seconds for meniscus to pass through intervals M_1M_2 and M_3M_4, respectively
h_1 and h_2 = heights in centimeters of mid-points of intervals M_1M_2 and M_3M_4, above bottom of capillary
d = density of latex in grams per cc.
R = radius of capillary in centimeters
L = length of capillary in centimeters
V = volume in cc. of each of the two intervals M_1M_2 and M_3M_4
g = acceleration of gravity in centimeters per second per second
T = temperatures in ° C.
η_T = coefficient of viscosity in centipoises at T° C.
η'_T = limiting coefficient of viscosity in centipoises at T° C.
η = coefficient of viscosity in centipoises at 25° C.
η' = limiting coefficient of viscosity in centipoises at 25° C.
F_0 = yield point at T° C. in grams per square centimeter

For purposes of latex testing and control the limiting coefficient of viscosity η' is of more importance than the true coefficient of viscosity, η. In fact, the quantities η' and F_0 completely specify the flow behavior of the latex in the range of practical interest for many purposes. Expressions for the calculation of η' and F_0 are given at this point.

$$\eta'_T = K_1 \frac{t_1 t_2}{t_2 - t_1}$$

where

$$K_1 = \frac{\pi R^4 g d (h_2 - h_1) \times 100}{8LV} \tag{1}$$

$$\eta' = \eta'_T[1 - 0.02(25 - T)] \tag{2}$$

$$F_0 = K_2 - K_3 \frac{\eta'_T}{t_2} \tag{3}$$

where

$$K_2 = \frac{h_2 R d}{2L}\ ;\ K_3 = \frac{V}{25\pi R^3 g}$$

Note.—The reason for introducing the limiting coefficient of viscosity, η', is that it is a constant for a given liquid of the latex type, whereas the true coefficient of viscosity is not. The introduction of the yield point, F_0, in the present sense and of η' is based upon the treatment of latex as an ideal plastic material in the sense of Bingham. This is not a true picture of the situation, but it is a sufficiently good approximation. A theoretical discussion of the behavior of such plastic bodies in the capillary viscometer is given by Bingham[1].

LAYING DOWN FILM OF RUBBER FROM LATEX, L-8

OUTLINE.—The purpose of specifying the manner of preparing a dried-down film of latex rubber is to obtain a material which can be directly subjected to the usual procedures for determination of manganese, copper, and acetone extract. A sheet of latex is spread onto a flat horizontal surface and slowly dried down to a transparent film by means of a current of warm air.

DETAILS.—Spread the latex to be dried down on a glass plate. Convenient amounts to use will be 1 cc. of normal latex per 6.45 sq. cm. (1 sq. in.) of surface or 0.5 cc. of concentrated latex per 6.45 sq. cm. If the film is to be used to determine acetone extract, carry out the drying process in a current of warm air, the temperature of which should not exceed 35° C. The length of time necessary to complete drying varies with different latices and with external conditions. Experience will indicate safe limits in practice.

It is advisable during the drying process to protect the film from contamination with atmospheric dirt. For this purpose it may be found convenient to use a jet of air which has been filtered through glass wool.

DETERMINING COPPER AND MANGANESE, L-9 AND L-10

These determinations are carried out on samples of dried-down film in exactly the same manner as directed in the Crude Rubber Committee's specifications for rubber[7].

The Crude Rubber Committee is coöperating with Sub-committee XI of Committee D-11 of the American Society for Testing Materials, which has adopted these procedures as tentative, but is planning certain revisions at the present time.

DETERMINING WATER-SOLUBLES, L-11

OUTLINE.—The procedure is to coagulate the ammonia-free latex with dilute acid and then to determine the water-soluble material remaining in the serum.

DETAILS.—By means of a weighing pipet, weigh 5 grams of the latex into a 400-cc. beaker and immediately add about 200 cc. of distilled water. Cover with a watch glass and boil on a hot plate until the volume has been reduced by one half. Transfer to a 200-cc. volumetric phosphoric acid flask (this type of flask has a wide neck and is easily cleaned) and make up to within about 200 cc. of the mark. Add 1 cc. of 0.1 per cent methyl orange indicator solution and add 1 *N* sulfuric acid from a buret until the red orange color, indicating a pH of about 4.3, is obtained and the rubber is well coagulated. Too much acid must not be added, as the sample will not coagulate well at an extremely low pH. Shake well to complete coagulation and make up to the mark. Filter the solution and pipet 100 cc. of the clear serum into a weighed evaporating dish. Evaporate to dryness on a steam bath and dry the residue in an air oven at 70° C. to constant weight.

The calculations are made as follows:

$$\text{Weight of solids} = \frac{\text{weight of sample} \times \%\ \text{solids}}{100}$$

$$\text{Weight of water-solubles} = \frac{\text{weight of soluble matter in 100 cc. of diluted serum} \times (200\text{-weight of solids})}{100}$$

From the weight of the total solubles subtract 0.0049 gram for every cubic centimeter of acid used and 0.001 gram for the weight of indicator. Then

$$\% \text{ water-solubles} = \frac{\text{corrected solubles weight}}{\text{weight of solids}} \times 100$$

The water-soluble matter in latex may be calculated roughly as the difference between the values obtained in the total solids and dry rubber content determinations. When an accurate value for the water-soluble material is not required, it may be calculated by means of this difference. However, in cases where it is important to know the water-soluble material accurately, it will be necessary to resort to the foregoing special procedure.

DETERMINING ACETONE EXTRACT, L-12

OUTLINE.—A dried-down latex film is extracted for 24 hours with pure acetone. The extract is dried to constant weight and the result expressed as percentage of extract based on the weight of dried film.

DETAILS.—Sheet the dried film out as thin as possible on a cold mill (the temperature here should not exceed 40° C), and use a 2-gram sample for extraction. Extract with freshly distilled acetone for 24 hours in an Underwriter's extraction apparatus. This extraction time will be sufficient for samples 0.0625 cm. (0.025 inch) or less in thickness. Evaporate the extract on a water or steam bath and dry to constant weight at 70° C. It is convenient to use for this purpose a flask which has been previously dried to constant weight at the same temperature. The result may be calculated as follows:

$$\text{Acetone extract in per cent} = \frac{\text{weight of extract}}{\text{weight of film sample used}} \times 100$$

Precaution. It is important to evaporate the acetone as specified over a water bath or a steam bath rather than over a hot plate, since overheating may occur and damage the extract even before all the acetone is removed.

NOTE ON MECHANICAL STABILITY OF LATEX

The Committee has omitted a procedure on mechanical stability of latex, since it was considered that the present tests had not been sufficiently developed and that their accuracy was not satisfactory. Work is in progress in the research laboratories of various companies for the purpose of developing a satisfactory test. It is hoped by the Committee that suggestions for a satisfactory mechanical stability test will be received from abroad or the United States.

The same remarks apply to chemical stability.

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[2] Clark, W. M., "Determination of Hydrogen Ions", 3rd Ed., Baltimore, Williams & Wilkins Co., **1928**, Chapters X, XII, XIV, XV, XVI.
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[4] *Ibid.*, Chapter XVI.
[5] Jordan, Brass and Roe, *Ind. Eng. Chem., Anal. Ed.* **9**, 182 (1937).
[6] Mooney and Ewart, *Physics* **5**, 350 (1934).
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A MECHANICAL OSCILLOGRAPH FOR ROUTINE TESTS OF RUBBER AND RUBBER-LIKE MATERIALS *

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OBJECT

The use of rubber and similar substances for vibration and shock isolation has created a need for tests of the mechanical properties involved in such service. At a given temperature, these properties are modulus under slow or practically static conditions, dynamic modulus, energy absorption by hysteresis loss and creep under a given dead load. In a previous paper the author presented a qualitative description of a method that might be used for these measurements[1]. In the present paper the method is developed in detail to permit the attainment of significant numerical data in fundamental physical units.

PRINCIPLES OF STATIC TESTS

Figure 1 shows the present form of the machine. As shown diagrammatically in Figure 2, the machine consists of a balanced lever supported at its center by

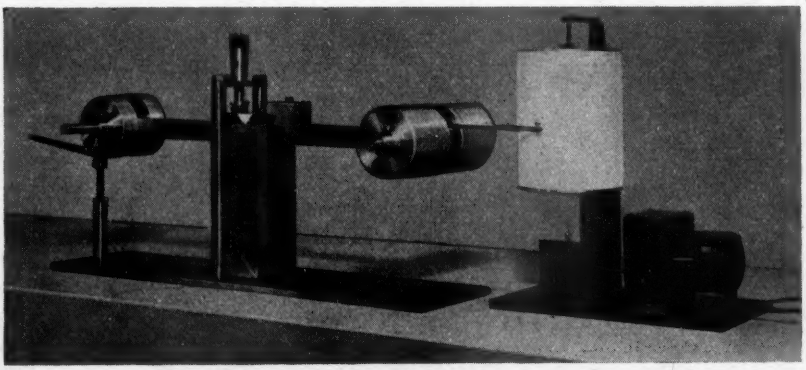

FIG. 1.—The oscillograph.

knife edges and a set of standard weights, which may be added to one end to compress a test-specimen *A* on the opposite side of the knife edges. A second knife edge and a stabilizing arm are introduced to render the compressing surfaces essentially parallel. Perfect balance of the lever may be obtained by adjusting the position of the counter-balance *B*. *A* pen arm extending from the heavy end of the lever automatically records deflections on the chart or oscillogram.

By an examination of Figure 2, it is obvious that the deflection of the rubber will be magnified in proportion to the lever ratio, which is 16.0 to 1.60. In other

* Transcribed from a preprint of a paper presented before the American Society for Testing Materials at the Atlantic City, N. J., meeting of June 26-30, 1939.

words a compression of 0.10 inch will be registered on the oscillogram as a vertical displacement of 1.00 inch.

The weight W in Figure 2 consists of several brass disks, each weighing 1.410 pound. The lever ratio for the weights is 10.0 to 1.60. Each weight on the end of the lever, therefore, results in a force of

$$1.41\text{ lb.}\times\frac{10.0}{1.60}=8.82\text{ lbs. on the test specimen}$$

The test-specimens are vulcanized in a cylindrical mold cavity $\frac{1}{2}$ inch high and $\frac{3}{4}$ inch in diameter. Their nominal cross sectional area is 0.441 square inch and the unit load resulting from each weight is, therefore:

$$\frac{8.82}{0.441}=20\text{ psi.}$$

It can be seen by reference to Figure 1 that the upper platen or loading surface of the machine can be raised or lowered by turning the micrometer

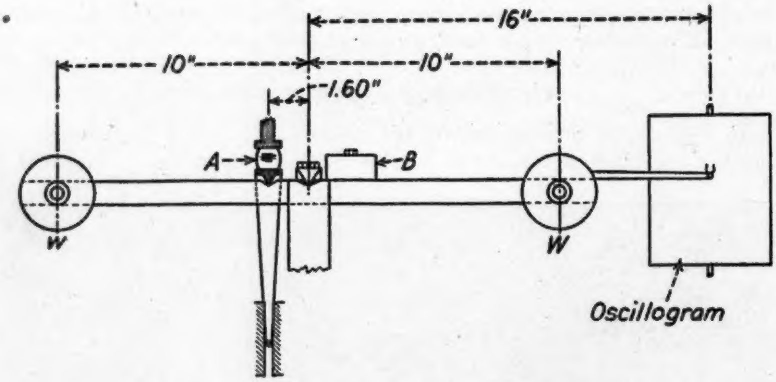

Fig. 2.—A diagrammatic description of the oscillograph.

head. This feature is important because it enables compensation to be made for slight variations of test-specimens from their nominal height and because test-specimens not of standard size can be tested.

ANALYSIS OF OSCILLATIONS

Figure 3 shows three positions of the apparatus necessary for an analysis of the oscillations consequent to sudden release of the unbalanced lever from an elevated position. The position of the lever corresponding to zero deformation of the test-specimen is shown in Figure 3 (a). When the lever is released, the heavy end falls, compressing the rubber, and during the ensuing time interval the oscillations occur. The deflections of the rubber are plotted autographically against time making a graph like those of Figure 4.

At the instant of release of the lever in the position of Figure 3 (a) the lever is accelerated by a torque equal to $(W\text{-}w)L$. In Figure 3 (b) the lever is shown at rest with the torque due to gravity counterbalanced by the torque resulting from compression of the test specimen.

That is:

$$(W-w)L=K'\frac{(h_0-h)}{(h_0)}l\ldots\ldots\ldots\ldots(1)$$

where W = weight on heavy end of lever,
w = weight on light end of lever,
h_0 = undeformed height of test-specimen,
h = height of pellet under equilibrium load, and
K' = assumed spring constant.

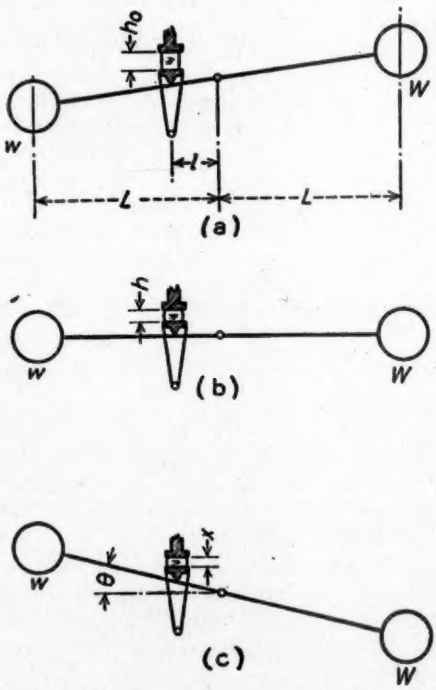

FIG. 3.—Three degrees of compression of a test-specimen.

(a) Undeformed.
(b) Static equilibrium under load.
(c) Any instantaneous deformation during a dynamic test.

At any instant during the vibrations the angular deflection from the equilibrium position can be represented by 0 in Figure 3(c) where x represents the corresponding height of the test-specimen. Therefore, at any instant, spring reaction on the loading platform $=K'\frac{(h_0-x)}{(h_0)}$ and the corresponding torque $=K'\frac{(h_0-x)}{(h_0)}l$. If I is the total moment of inertia of the lever and the weights about the main fulcrum and $\frac{d^2\theta}{dt^2}$ is the angular acceleration:

$$I\frac{d^2\theta}{dt^2}=(W-w)l-K'\frac{(h_0-x)}{(h_0)}l\ldots\ldots\ldots\ldots(2)$$

Substituting Equation 1 in Equation 2

$$=K'\frac{(h_0-h)}{(h_0)}l-K'\frac{(h_0-x)}{(h_0)}l \qquad (3)$$

$$=K'l\frac{(x-h)}{(h_0)}$$

or

$$I\frac{d^2\theta}{dt^2}-K'l\frac{(x-h)}{(h_0)}=0 \qquad (4)$$

If the static equilibrium position of the lever is approximately horizontal, for small angles:

$$\theta=\frac{h-x}{l}$$

$$\frac{d\theta}{dt}=-\frac{1}{l}\frac{dx}{dt}$$

$$\frac{d^2\theta}{dt^2}=-\frac{1}{l}\frac{d^2x}{dt^2} \qquad (5)$$

Substituting Equation 5 in Equation 4:

$$\frac{-I}{l}\frac{d^2x}{dt^2}-K'l\frac{(x-h)}{(h_0)}=0 \qquad (6)$$

$$\frac{d^2x}{dt^2}+\frac{K'l^2}{I}\frac{(x-h)}{(h_0)}=0 \qquad (7)$$

which is the equation of motion for the oscillograph for test-specimens obeying Hooke's law with $K'=$a constant. Let $u=x-h$.

Then:

$$\frac{d^2u}{dt^2}+\frac{K'l^2}{Ih_0}u=0 \qquad (8)$$

For this simple harmonic motion:

$$f=\text{frequency}=\frac{1}{2\pi}\sqrt{\frac{K'l^2}{Ih_0}}$$

$$\text{so } K'=\frac{4\pi^2h_0}{l^2}If^2 \qquad (9)$$

For standard test-specimens $\frac{1}{2}$ inch by $\frac{3}{4}$ inch in diameter:

$$K'=\frac{4\pi^2(0.50/12)}{(1.6/12)^2}If^2$$

$$=92.5\,If^2\text{ lbs.}$$

The area of the test-specimen, however, is 0.441 square inch, so:

$$K=\frac{92.5}{0.441}If^2=210\,If^2\text{ psi.} \qquad (10)$$

The moment of inertia of the lever and the weights of the particular machine under discussion is given by:

$$I = 0.0813 + n \times 0.0307 \text{ slug ft.}^2 \quad \ldots\ldots\ldots\ldots (11)$$

where n = the total number of weights used in a given test.

The frequency of vibration is calculated from the chart by dividing a whole number of cycles by the elapsed time in seconds.

IMPACT ENERGY AND RESILIENCE

In the beginning of a dynamic test and at the instant the lever is released, the lever possesses its maximum potential energy by virtue of the elevation of the heavy end. As the weight falls, part of the potential energy is converted into heat in the test-specimen, due to internal friction, and part is stored in the test-specimen by elastic compression. At the point B on the first downward sweep of the oscillation record in Figure 4(a) the lever is undergoing a reversal of direction and is momentarily stationary. Since this is the lowest point of the vibration the potential energy of the lever is a minimum. The vertical component of the line AB is an accurate measure of the energy of the impact. Suppose the vertical length of the line AB were 1.00 inch, due to the impact of one weight on the end of the lever. Then the distance through which the weight has fallen is $\frac{10.0}{16.0} \times 1.00 = 0.625$ inch, and the corresponding energy of impact is 0.625×1.41 lbs. = 0.882 in.-lbs. The volume of the test-specimen is $0.500 \times 0.441 = 0.2205$ cu. in. Hence, the energy of a single weight corresponding to a 1.00 inch vertical distance on the chart is $\frac{0.882}{0.2205} = 4.00$ in.-lbs. per cu. in. of vulcanizate. Hence energy transfer in fundamental units can be calculated from maximum and minimum points on the oscillogram by the simple formula:

$$\text{Energy} = 4n' \times \text{vertical distance in inches on oscillogram} \quad \ldots\ldots (12)$$

where n' is the number of unbalanced weights on the heavy end of the lever.

It will be noted that every rising line on the chart represents return of potential energy to the lever. Hence percentage resilience may be determined by taking the ratio of the rebound height to the impact height. That is from Figure 4(a).

$$\text{Percentage resilience} = \frac{BC}{AB} \times 100$$

ROUTINE MEASUREMENTS

It is now possible to consider specific details of the test for the measurement of the following static and dynamic characteristics:

1. Static Characteristics

(a) Compression loading and unloading characteristics. Load is given in pounds per square inch, deflections in inches or percentage.

(b) From the above data, energy transfers may be calculated in inch-pounds, or inch-pounds per cubic inch of stock.

(c) Creep in inches or per cent under a given dead load (load range from 20 to 280 psi.).

(d) Set in inches or percentage.

2. Dynamic Characteristics

(*a*) Energy absorption of impact loads in inch pounds per cubic inch of stock.
(*b*) Percentage resilience under known load, deflection range and frequency.
(*c*) Effective dynamic modulus in pounds per square inch.
(*d*) A limited adjustment of the frequency of the test is possible.

Figures 4 and 5 illustrate the method of obtaining the data and converting it into customary forms. Figure 4(*a*) is the data sheet obtained from a

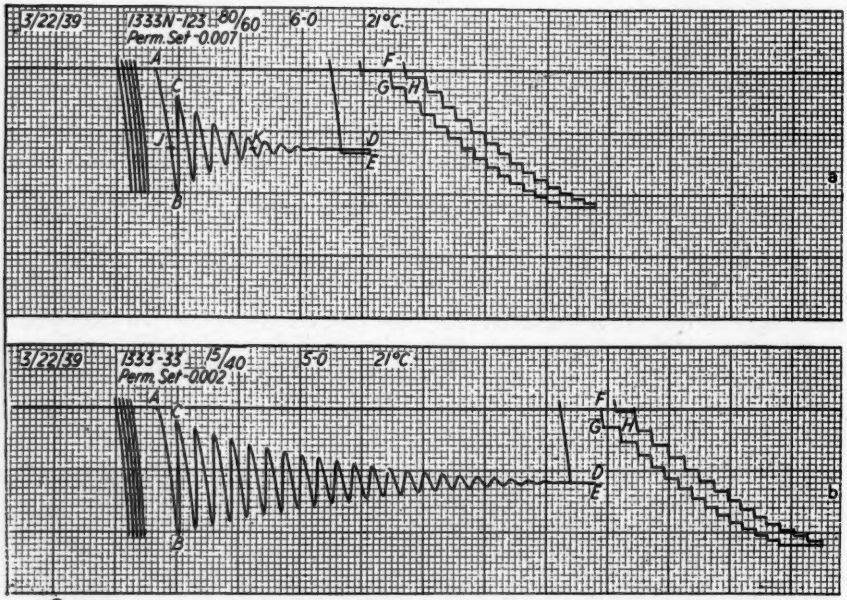

Fig. 4.—Typical oscillograms for neoprene (*a*) and rubber (*b*).

Neoprene Type E compound (1) and Figure (*b*) is a data sheet obtained for a similar rubber compound (2):

(1)	Neoprene Type E	100.
	Extra light calcined magnesia	5.
	FF wood rosin	2.
	Phenyl-β-naphthylamine	2.
	Sulfur	1.
	Litharge	3.
	Press cure—80 min. at 141.7 C. (287 F.)	
	Durometer A hardness—41	
(2)	Smoked sheets	100.
	Zinc oxide	5.
	Stearic acid	1.
	Phenyl-α-naphthylamine	1.
	Tetramethylthiuram monosulfide	0.3
	Sulfur	3.
	Cure—15 min. at 152.8 C. (307 F.)	
	Durometer A hardness—39	

In Figure 5 curves (*a*) and (*b*) are derived from the oscillograms shown in Figures 4(*a*) and (*b*), respectively.

Referring to Figure 4(a), the reference line is traced around the recording drum as the first step in any test. This is done with the heavy end of the lever held in the position corresponding to zero deformation of the test-specimen by allowing the recorder drum to rotate through one revolution. Reproducible results are obtained only on test-specimens which have been through several cycles of loading and unloading. For that reason, before beginning the oscillogram proper, several complete sets of oscillations are run but are recorded only as arcs as shown on the left end of the oscillogram in Figure 4(a). It will be seen that the lower end of each of these arcs can be compared with its predecessor to observe whether or not the same compression is being obtained on successive trials. It is, of course, necessary that the weights used for the conditioning cycles be the same as those to be used in the test. For the oscillogram of Figure 4(a) six weights were used on the heavy end imposing an average load of 120 psi. on the test-specimen.

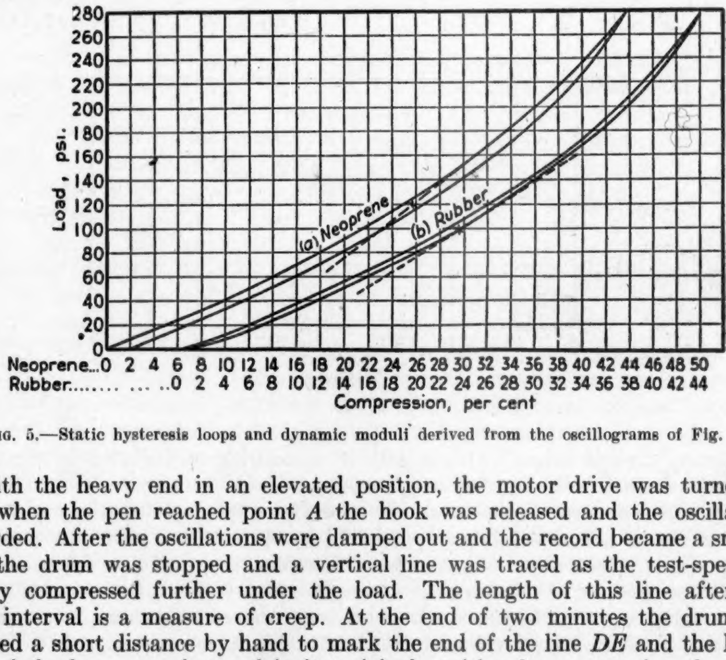

FIG. 5.—Static hysteresis loops and dynamic moduli derived from the oscillograms of Fig. 4.

With the heavy end in an elevated position, the motor drive was turned on and when the pen reached point A the hook was released and the oscillations recorded. After the oscillations were damped out and the record became a smooth line the drum was stopped and a vertical line was traced as the test-specimen slowly compressed further under the load. The length of this line after any time interval is a measure of creep. At the end of two minutes the drum was rotated a short distance by hand to mark the end of the line DE and the heavy end of the lever was fastened in its original position by re-engaging the hook. Since creep had occurred, the pellet no longer filled the distance between the two loading platforms. By turning the micrometer head, the upper platen was brought down to the new height of the pellet. The distance it moved was recorded as the set. In the test under discussion, this was recorded as 0.007 inch. The creep which occurred during the same time interval of 2 minutes was 0.006 inch. There is no apparent reason why these two figures should check accurately, since one figure represents change in height under load and the other change in height of the unloaded pellet. After measuring the set the micrometer was returned to its former setting.

Measurements of creep and set over relatively short time intervals can be of only limited usefulness. A few comparisons between the short-time drift and

drift over longer periods of time have indicated, however, that in a given class of compositions there may be a rough correlation between short-time drift and the total creep which would occur over longer periods of time. By plotting creep against time, curves of the type shown in Figure 6 may be obtained.

After completion of the creep test, the drum was then rotated so that the pen rested on point *F*, and at this point all weights were removed from the machine. The hook was then held back, and one weight was added to the pen end of the lever. Compression under the load of 20 psi. is represented on the chart (Figure 4(*a*)) by the line FG, after which rotation of the drum by hand caused the line *GH* to be drawn. Weights were added stepwise in this way to the full load capacity of the machine, 280 psi. and were then removed one by one in order to obtain unloading data. The deflections corresponding to these loads were replotted on load compression axes to obtain the hysteresis loop shown in Figure 5(*a*).

From the static loading and unloading curve thus obtained, it is possible to calculate the energy in inch pounds per cubic inch of stock required for compres-

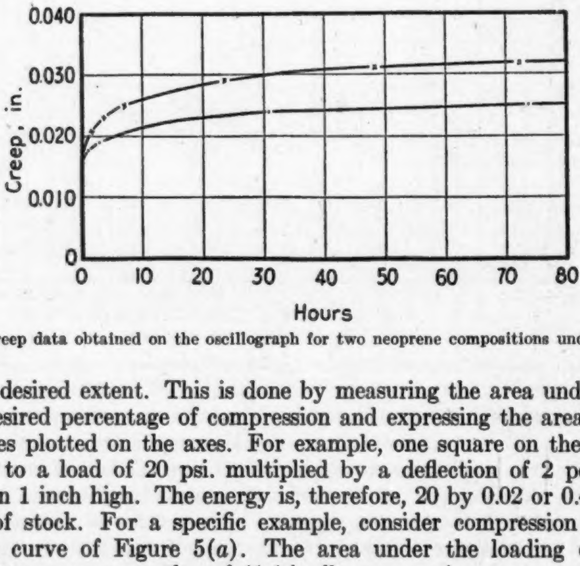

FIG. 6.—Creep data obtained on the oscillograph for two neoprene compositions under 240 psi.

sion to any desired extent. This is done by measuring the area under the curve up to the desired percentage of compression and expressing the area in terms of the quantities plotted on the axes. For example, one square on the curve sheet corresponds to a load of 20 psi. multiplied by a deflection of 2 per cent in a test-specimen 1 inch high. The energy is, therefore, 20 by 0.02 or 0.4 in.-lbs. per cubic inch of stock. For a specific example, consider compression of 40.4 per cent on the curve of Figure 5(*a*). The area under the loading curve up to this point gives an energy value of 41.4 in.-lbs. per cu. in.

Again referring to Figure 4(*a*), the length of the line *AB* can be used to calculate the energy of the impact which caused the compression of 40.4 per cent. This calculation, based on Equation 12, is 4 by 6 by 2.02=48.4 in.-lbs. per cubic inch of stock. If the static characteristics of this Neoprene and its characteristics at the frequency of the dynamic test are the same, the impact energy should be the same as that previously calculated from the static load-compression curve. There is a discrepancy, however, and the dynamic energy is greater than that calculated from the static curve. The percentage resilience of the compound under these load conditions can be calculated from the ratio of the vertical heights of the lines *BC* and *AB*. This figure is 1.58 divided by 2.02=78.2 per cent. It should be noted, however, that this value of the resilience was determined for the compound at 21 C at the stated load, deflection range and frequency, and that a change in one of the variables might change the resilience.

We now come to the calculation of effective modulus in pounds per square inch. The calculation of frequency in this case is based on 5 cycles and on elapsed time of 1.35 second, so that $f=5$ divided by $1.35=3.70$ cycles per second, where 1.35 is the distance JK in Figure 4(a). Therefore, f^2 is 13.8 and from Equation 11, $I=0.0813+6\times0.0307=0.2655$ slug ft.^{2} Substituting in Equation 11, $K=210\times0.2655\times13.8=769$ psi. If the static and dynamic characteristics of Neoprene were the same, this calculated value for the dynamic modulus should be numerically equal to the slope of the tangent drawn to the static load-compression curve shown in Figure 5(*a*) at the load of 120 psi. For purposes of demonstration, however, it is more convenient to plot the value of K on the load-compression curve by drawing a straight line of the proper slope at the point corresponding to the point D in Figure 4(*a*). At the point D the load is 120 psi. and the compression in 25.6 per cent. This point is indicated on Figure 5(*a*) by the cross, and the dotted line represents the dynamic modulus. Here it can be seen that the effective dynamic modulus is greater than the static modulus represented by the slope of the load-compression curve at 120 psi.

The frequency of the test is determined by the value of K and the inertia of the machine. At a given load, K cannot be independently varied, but within a restricted range the inertia of the machine can be varied. For example, for the test of Figure 4(*a*) there were six weights on one end of the machine and no weights on the other. The same load could have been obtained by using ten weights on one end of the machine and only four on the other. This would have increased the inertia of the machine and decreased the frequency of the test. For brevity, additional data are not given here. It appears, however, that a greater difference in frequency must usually be used than is possible by this method in order to measure the effect of test frequency on the value of the dynamic modulus.

For simplicity the foregoing discussion has been based upon the test of Neoprene illustrated in Figure 4(*a*). It will be understood that the test is equally applicable to rubber and other rubber-like materials. For example, similar calculations can be made for the data in Figure 4(*b*) for rubber. The static and dynamic moduli are illustrated in Figure 5(*b*), and it is significant that they are within experimental error the same. In this respect, they differ from the results for Neoprene. In further confirmation of the difference between the Neoprene compound and the rubber compound, the energy values also correspond for the static and dynamic tests. The energy imparted to the rubber by the impact in Figure 4(*b*) is: $4\times5\times2.05=41.0$ in.-lbs. per cubic inch of stock. The area under the curve up to 41.0 per cent compression gives 40.4 in.-lbs. per cubic inch of stock. This also seems to be in almost perfect agreement with the value obtained from the dynamic test.

It is likely that the difference between static and dynamic characteristics are linked in some specific way with the damping factor of a given compound: that compounds having high resilience will show the least difference between static and dynamic characteristics and that the discrepancy between the two is in general widened as the resilience decreases. It is important to emphasize, however, that the value K is given as an effective dynamic modulus but not an actual physical modulus. It is in a sense a fictional quantity. Actually the oscillations do not occur over a linear load-compression relationship except for small deflections near zero load and for heavily reinforced compositions. However, the dynamic modulus is a quantity which has greater significance with respect to vibration calculations than any value that could be taken from the static curve.

Brevity requires that discussion of certain details be restricted to brief statements. The mathematical derivations, for example, have been confirmed by tests of a calibrated coil spring. With respect to the molded test-specimens, the use of nominal rather than actual dimensions seems justified since mold shrinkage is characteristic of a given vulcanizate, either in the preparation of test-specimens or in the manufacture of articles in production. Test-specimens can be prepared in other ways than molding as special circumstances may require. Slight errors in testing have been noticed due to frictional losses between the surface of the test-specimen and the compressing platens. These errors may be eliminated by using test-specimens adhered to metal end plates.

CONCLUSIONS

The oscillograph described has been developed primarily as a laboratory instrument to evaluate rubber and Neoprene compounds for mechanical applications. It is complete in itself as a means of measuring all of the quantities inherently involved in such service in units which are understandable to rubber technologists and mechanical engineers alike. It is hoped that it may serve its purpose by bringing into closer cooperation those who make and those who use rubber springs. The details of the test have been carefully developed, and it is expected that the machine and standard test-specimen described will not need essential modification for routine use. However, enough background has been given so that the machine may be modified in accordance with definite principles in order to gain greater load capacity if required. The test has been restricted thus far to compression. The author expects to adapt the machine to tests in shear, and by correlation between shear data and compression data to obtain figures capable of substitution in relationships already offered by other investigators[2] for calculations in the applications and design of rubber springs. This field of calculation is complicated and in an early state of development, but by the use of the oscillograph it should be easier to obtain the quantities of information required to clarify our understanding of the mechanical characteristics of rubber-like materials within the range of deformation encountered in structural use.

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NEOPRENE CEMENTS *

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A solution of Neoprene resembles those of other colloids in showing a marked increase in viscosity with increase in concentration. The viscosity of a Neoprene solution of any given concentration depends on the plasticity of the Neoprene used in the preparation of that solution, much the same as the viscosity of a natural rubber solution depends on the state of degradation of the rubber. The viscosity of a Neoprene solution, like that of natural rubber, also varies with the type of solvent.

A study of the factors affecting the viscosity and stability of Neoprene-benzene cements has been made on cements prepared from uncompounded and compounded Neoprene. Neoprene Type E was compounded with 10 parts of light calcined magnesia, 5 parts of zinc oxide and 5 parts of FF wood rosin per 100 parts of Neoprene. With Neoprene Type G the use of rosin is unnecessary. The cements were prepared by dispersing the Neoprene or Neoprene compounds in thiophene-free benzene by slowly rotating the container until a homogeneous dispersion was obtained. Concentrations are expressed on the total solids basis. Samples of the smooth dispersions were transferred to Gardner-Holdt bubble tubes, and the viscosity was measured at 76° F (24.4° C). The bubble tubes were then stored at 120° F (48.9° C), and the viscosity was measured at intervals of 1 to 2 weeks until the more concentrated dispersions had increased in viscosity by several hundred per cent or gelled particles had appeared. This method of measuring the viscosity was considered sufficiently accurate for the purpose, and it had the advantage that no solvent was lost during storage at the elevated temperatures. Portions of the samples were also stored for several months at room temperature in larger containers. Cements were considered stable until they had increased more than 100 per cent in viscosity, or until gelled particles appeared or complete gelation occurred.

EFFECT OF CONCENTRATION

Data illustrating the influence of concentration on the viscosity of fresh cements are shown in Figure 1. Neoprenes Type E with a plasticity-recovery of 84-4 and Type G with a plasticity-recovery of 113-10 were used in preparing these solutions. The plasticity-recovery numbers in 0.001 inch were determined at 80° C. on 2-cc. pellets with the Williams parallel plate plastometer[2].

The Type G had been plasticized by milling under water according to the method recommended for obtaining water plasticized Type GW[1].

The viscosity measurements were made in Gardner-Holdt bubble tubes. The conversion to centipoises was made by means of a curve drawn from results obtained with standard solutions in a similar set of tubes. The results are believed to be accurate within 5-10 per cent.

It is apparent that the viscosity of a Neoprene Type E cement is changed very little by compounding with curing agents, but that the viscosity of the more concentrated compounded Type G cements is definitely less than the corresponding uncompounded cements. The difference between curves *A* and *B* is partly

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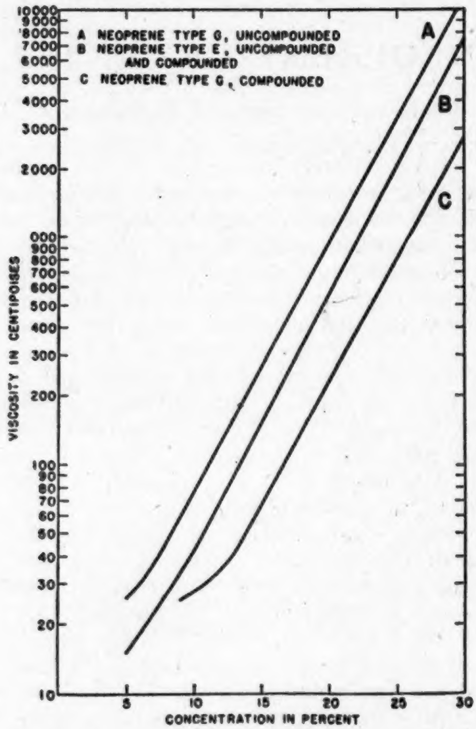

FIG. 1.—Effect of concentration on viscosity of neoprene cements.

TABLE I

NEOPRENE TYPE E CEMENTS IN BENZENE

Concentration, %	Bubble tube viscosity at 76° F, seconds								
	After weeks' aging at 120° F:								After 5 mo. at room temp.
	0	1	2	3	4	6	8	10	
UNCOMPOUNDED CEMENTS									
5	0.8	0.8	0.7	0.7	0.7	0.7	0.8	0.8	0.8
10	1.2	1.2	1.2	1.2	1.1	1.2	1.2	1.2	1.0
15	2.7	2.4	2.2	2.2	2.4	2.2	2.4	2.8	3.2
20	7.2	7.0	6.2	6.0	6.0	6.2	6.6	8.0	11.4
25	23.8	23.8	22.5	—	21.5	24.0	28.4	—	40
30	108	99	92	105	120	Gel	—	—	114
COMPOUNDED CEMENTS [a]									
5	0.6	0.7	0.7	0.8	0.7	0.8	0.8	0.8	1.0
10	1.0	1.0	1.0	1.0	1.2	1.0	1.0	1.0	1.2
15	2.2	2.4	2.2	2.4	2.4	2.7	3.2	4.2	2.8
20	7.3	7.3	8.0	14	10.5	14	20	45	12
25	25.4	28.4	32.5	67	Gel	—	—	—	65
30	110	115	180	300	Gel	—	—	—	175

[a] 100 Neoprene, 10 light calcined magnesia, 5 zinc oxide, 5 FF wood rosin.

due to the fact that this particular Type G sample was somewhat less plastic than the Type E.

The measurements obtained with these Type E cements, after aging at 120° F and at room temperature, are given in Table I.

Cements of uncompounded Neoprene Type E up to 25 per cent concentration are stable for 8 weeks at 120° F or for 5 months at room temperature. The compounded 20 per cent cements were stable for 5 months at room temperature but for only 6 weeks at 120° F. The more concentrated cements are definitely less stable.

TABLE II

NEOPRENE TYPE G CEMENTS IN BENZENE

Concentration, %	Bubble tube viscosity at 76° F, seconds: After weeks' aging at 120° F: 0	1	2	3	4	6	8	10	After 5 mo. at room temp.
	UNCOMPOUNDED CEMENTS								
5.0	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
9.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.2
13	2.4	2.2	1.6	1.5	1.2	1.4	1.4	1.6	1.8
16.7	6.2	5.2	3.2	2.8	2.8	3.4	4.6	Gel	4.0
20	7.0	4.8	4.0	3.2	—	4.0	5.5	—	9.8
25	30.6	17.6	14.5	15.5	—	23.0	45	—	50
30	161.5	57.5	70.0	145	265	Gel	—	—	47
	COMPOUNDED CEMENTS [a]								
5.0	0.8	0.7	0.7	0.7	0.8	0.8	0.8	0.8	0.8
9.0	0.8	0.8	0.8	0.8	1.0	0.8	1.2	2.8	1.0
13.0	1.0	1.0	1.2	1.4	1.8	6.4	Gel	—	1.2
16.7	1.6	1.6	1.8	3.2	6.0	Gel	—	—	2.6
20	7.2	10.0	25.5	Gel	—	—	—	—	50
25	13.4	25.5	275	Gel	—	—	—	—	65
30	31.0	Gel	—	—	—	—	—	—	Gel

[a] 100 Neoprene, 10 light calcined magnesia, 5 zinc oxide.

Similar data for Neoprene Type G cements are given in Table II. On aging the more concentrated uncompounded Type G cements, the viscosity decreased quite markedly for some time before it started to increase. This phenomenon did not appear in the case of the compounded cements, although it should be noted that the viscosity of the more concentrated compounded cements is lower than that of the similar uncompounded cements. These compounded cements show an increase in viscosity on aging, without a preliminary decrease. This is analogous to the change in plasticity of compounded and uncompounded Neoprene Type G on storage. The uncompounded Type G cements were nearly as stable as the corresponding Type E cements, but the compounded Type G cements apparently are less than stable than Type E cements.

EFFECT OF ADDED COMPOUNDS

The decrease in the viscosity of compounded Neoprene Type G cements over the similar uncompounded cements is believed to be due to the influence of the alkaline magnesia. Similar effects have been noted with alkaline organic materials. Data obtained with cements made from Neoprene Type G to which 2 per cent diphenylguanidine had been added, are shown in Table III.

A comparison of Tables II and III shows that the addition of diphenylguanidine to the uncompounded cements resulted in a marked decrease in the original viscosity. There is no corresponding decrease in the viscosity of the compounded cements with the addition of diphenylguanidine. The addition of diphenylguanidine rendered the more concentrated cements less stable at 120° F., but the stability as measured at room temperature was very little affected.

Table III

Neoprene Type G Cements in Benzene + 2 Per Cent Diphenylguanidine

Concentration, %	Bubble tube viscosity at 76° F, seconds: After weeks' aging at 120° F: 0	1	2	3	4	6	8	10	After 5 mo. at room temp.
				Uncompounded cements					
5	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
9	0.8	0.8	1.0	1.0	1.0	1.0	1.2	1.8	0.8
13	1.2	1.2	1.2	1.6	2.4	13.4	Gel	—	1.1
16.4	1.8	1.8	2.2	4.2	8.2	Gel	—	—	2.0
30	28.8	39.5	Gel	—	—	—	—	—	45
				Compounded cements					
5	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
9	0.8	0.8	0.8	0.8	1.0	1.8	Gel	—	1.0
13	0.9	1.0	1.2	2.5	Gel	—	—	—	1.2
16.4	1.6	1.6	4.2	Gel	—	—	—	—	2.2
30	30	45	Gel	—	—	—	—	—	Gel

Table IV

Neoprene Type E Cements in Benzene + 2 Per Cent Diphenylguanidine

Concentration, %	Bubble tube viscosity at 76° F, seconds: After weeks' aging at 120° F: 0	1	2	3	4	6	8	10	After 5 mo. at room temp.
				Uncompounded cements					
5	0.8	0.8	0.7	0.7	0.7	0.7	0.8	Gel	0.8
10	1.2	1.2	1.2	1.2	1.0	1.2	1.2	Gel	1.1
15	3.2	3.2	3.2	3.0	3.2	2.2	2.4	4.2	3.0
20	13.0	13.2	13.2	Gel	—	—	—	—	Grainy
30	113.0	126	120	130	Gel	—	—	—	117
				Compounded + 2 per cent D. P. G. cements					
5	0.6	0.7	0.7	0.8	0.8	0.8	0.8	0.8	1.0
10	1.0	1.0	1.0	1.0	1.2	1.0	1.0	1.0	1.2
15	2.6	2.4	2.2	2.4	2.4	2.6	2.8	3.2	2.4
20	8.0	8.0	8.2	8.0	9.0	9.4	10.0	16.0	7.8
30	105.0	135.0	160	190	290	Gel	—	—	115

Similar data for Neoprene Type E containing 2 per cent of diphenylguanidine are given in Table IV.

A comparison of Tables I and IV shows that the addition of diphenylguanidine has very little effect on the original viscosity of the Type E cements. It appears to render the uncompounded Type E cements less stable but to improve somewhat the stability of the corresponding compounded cements.

Since it would be desirable to improve the stability of the more concentrated cements, the effect of a number of compounds was investigated. Some of them had comparatively little effect; others, such as catechol, caused the gelation of the cements. The results obtained with two compounds which actually stabilized the cements are shown in Figure 2. Tricresyl phosphate appears to act as a diluent and improves the stability in proportion to the amount used. Sodium

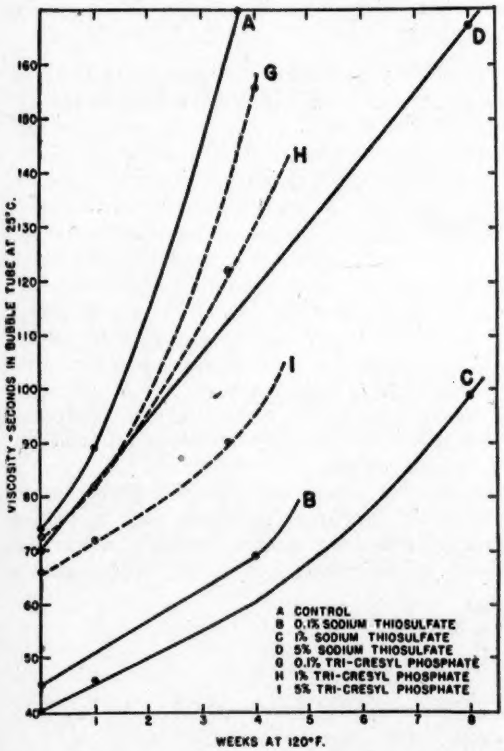

Fig. 2.—Effect of various compounds on compounded 30 per cent cements (Neoprene type E).

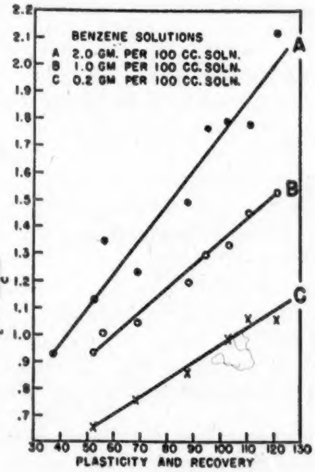

Fig. 3.—Relation of plasticity + recovery to intrinsic viscosity of Neoprene.

thiosulfate produces a much more marked effect, and 1 per cent gives appreciably greater stability than either 0.1 or 5 per cent.

A series of experiments with benzene of different purity showed no significant variations. However as Table V shows, the moisture content may have a marked effect on the viscosity of the more concentrated cement. It had comparatively little effect on the 10 per cent cements.

VISCOSITY OF DILUTE CEMENTS

The relative viscosity of dilute cements, prepared from a number of different samples of Neoprene, was determined at 30° C in an Ostwald type viscometer, which flowed a volume of 7.2 cc. through a capillary 0.816 mm. in diameter and 4.5 cc. long under a mean head of 9.9 cc. of solution. From these measurements

the intrinsic viscosity has been reported. The intrinsic viscosity $[\eta]$ is defined by the expression,

$$[\eta] = (\eta r - 1)/c \text{ (as } c \text{ approaches 0)}$$

where $[\eta r]$ = viscosity of solution relative to that of solvent
c = concentration, grams/per 100 cc. of solution.

Data for solutions containing 2.0, 1.0 and 0.2 gram per 100 cc. of solution are shown in Figure 3. These data show that $[\eta]$ increases materially with increasing

TABLE V

INFLUENCE OF WATER ON VISCOSITY OF COMPOUNDED NEOPRENE TYPE E BENZENE CEMENTS

	Bubble-tube viscosity, in sec., at 76° F after weeks aged at 120° F:		
	0	5	0
	10% cements		
Water, %			30% cements
0	1.2	4	88
0.1			90
0.4			223
0.5, 0.7	2.0	3	Too viscous to measure
1.0	2.2	3.2	Too viscous to measure
3.0	3.2	3.2	Too viscous to measure

concentration, and that there is an approximately linear relation between $[\eta]$ and the plasticity plus recovery of various samples of Neoprene.

If the conclusions of Staudinger and his school are accepted, these results indicate that the molecular weight of the Neoprene decreases with increasing plasticity. Calculations of the apparent molecular weight, from the sedimentation equilibrium and intrinsic viscosity measurements by J. B. Nichol of the

TABLE VI

EFFECT OF SOLVENTS ON VISCOSITY

	Plasticity-recovery	Concn., G. per 100 cc.	$[\eta^r]$ in benzene	$[\eta^r]$ in amyl chloride
Neoprene	105–5	2.0	4.55	3.41
		1.0	2.45	1.88
		0.2	1.21	1.13
	50–2	2.0	3.24	2.41
		1.0	1.93	1.55
		0.2	1.13	1.09
Rubber (3)	—	2.0	1.24	7.74
		1.0	4.17	2.72
		0.25	1.47	1.21

du Pont Experimental Station, also indicate that the more plastic Neoprene has the lower apparent molecular weight. He obtained apparent molecular weights varying from about 200,000 to about 500,000, using samples of this same general plasticity range.

As indicated by Williams[3], the variation in the results obtained with different solvents must be taken into consideration in drawing theoretical conclusions. The effect of solvents noted for rubber is also found in the case of Neoprene, as Table VI shows.

The relative viscosity of Neoprene dissolved in amyl chloride is definitely lower than that of Neoprene dissolved in benzene. Similar measurements, made with natural rubber by Williams, are included for comparison. In both cases the specific viscosity is higher in benzene than in amyl chloride, but for the same concentration, the effect is much greater with natural rubber than with Neoprene. This difference might be interpreted as indicating that the Neoprene was solvated to a less extent than the natural rubber.

SUMMARY

Data are presented regarding the viscosity and stability of Neoprene cements in benzene containing up to 30 per cent total solids. Although the more concentrated cements have only limited stability, especially at elevated temperatures, those up to 15 per cent concentration are sufficiently stable for practical purposes. Cements made from Neoprene Type G are slightly less stable than those made from Neoprene Type E, but up to 17 per cent concentration are still usable after 5-month storage at room temperature. Compounding somewhat reduced the stability of concentrated cements. The addition of sodium thiosulfate during compounding improves the stability of Neoprene Type E cements. Diphenylguanidine lowers the viscosity of Neoprene Type G cements but renders them slightly less stable. The viscosity of cements for any given solvent or concentration varies with the plasticity of the Neoprene. The variation of the intrinsic viscosity determined in different solvents makes the calculations of molecular weights from this type of data extremely uncertain.

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ADHESION OF NEOPRENE TO METAL *

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The increasing commercial demand for vulcanized articles in which adhesion between Neoprene and metal is essential has encouraged a comprehensive study of the adhesion problem. The A. S. T. M. standard procedure (Designation D429-36T) was examined critically as a possible means of evaluating adhesion to metal, but it was found lacking in respect to control of both the pressure on the vulcanizate and the flow in the mold. To control and measure these factors, special equipment (described later) was developed. Many methods of obtaining adhesion to metal were investigated, but only two of them with which outstanding results were obtained are reported. These are adhesion directly to brass or to brass plate, and adhesion to a variety of metals through the use of properly selected cements containing chlorinated rubber.

TEST-PIECES

The test-pieces employed throughout were cylinders nominally 1.600 inches in diameter and $\frac{7}{8}$ inch high. These consisted of two metal disks, $\frac{3}{8}$ inch thick,

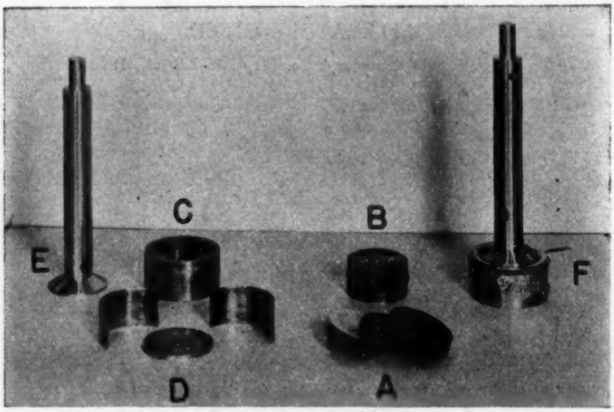

FIG. 1.—Special mold equipment.

bonded to each other through a layer of vulcanizate $\frac{1}{8}$ inch thick, vulcanized in special equipment described here and employing the adhesive method under test in each case. This thickness of vulcanizate was selected rather than the A. S. T. M. thickness of $\frac{1}{2}$ inch to obtain a greater range of flow conditions. Figure 1*A* shows the parts of the test-pieces before vulcanization, *B* a test-piece after vulcanization. Four threaded holes in the back of each metal disk provided a means of holding the samples in the test machine. The metal surfaces were cleaned by washing with benzene, followed by polishing on garnet paper and crocus cloth. Surfaces mechanically polished in this way were adopted as standard in the belief that they can be duplicated more readily than pickled or sandblasted surfaces.

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THE MOLD

A single-cavity plunger type mold was developed for optimum heat transfer during curing and for removal of test-pieces without resort to lubricants. It is shown in disassembly in Figures 1*C* and *D*. *C* is a hollow cylindrical shell which is the body of the mold. *D* shows a removable bottom and two halves of a split sleeve which lines the mold. *E* shows the plunger, and *F* the entire mold assembled with a test piece ready for vulcanization. The holes in the shank of the plunger are provided to increase the area in contact with the heating medium during cure. Provision is made to wire the mold together to facilitate handling during insertion in the press. It should be noted, however, that glycerol used in the bath can easily penetrate into the open spaces of the mold, and for that reason it has been general practice to seal the top of the mold with a covering of tin foil as shown in *F*. The openings through which glycerol might penetrate into the bottom of the mold are very small, and special precautions there were found unnecessary. The only function of the tin foil covering is to keep glycerol out of the mold until

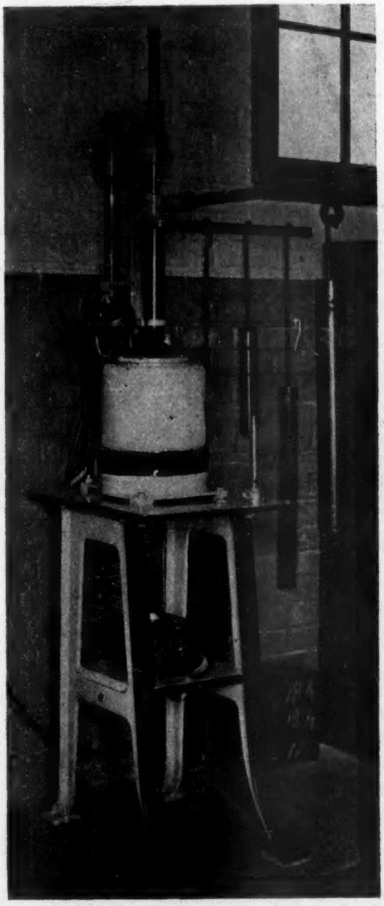

Fig. 2.—General view of mechanical press.

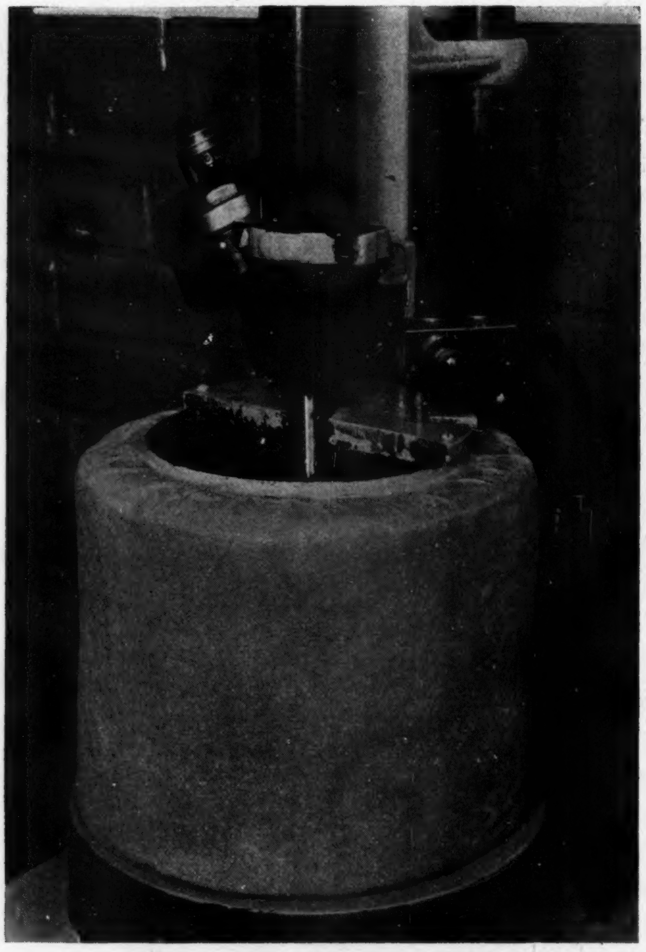

FIG. 3.—Close-up of glycerol bath.

pressure is applied on the test-piece, after which glycerol is effectively excluded from the interface between the vulcanizate and the metal.

Removal of the test-piece from the mold after cure is accomplished by pushing on the false bottom, thereby forcing out the test-piece and the split sleeve. The split sleeve is then stripped away from the test-piece. All parts of the mold, except the split sleeve, are made of 18-8 stainless steel to prevent rusting. The split sleeve, which must occasionally be replaced as it loses its original form, is made of low-carbon steel.

GLYCEROL BATH AND PRESS

The frame of a discarded drill press was converted into a mechanical press, as shown in Figures 2 and 3. The platen of the press is raised from the floor of

the bath and is completely surrounded by glycerol. The temperature control during vulcanization is as precise as the control of the electric heating element. Temperature variations appear to be of the order of $\pm 0.1°$ C; and closer control, though easily attainable, was not considered necessary. Pressure on the vulcanizate is determined by the ratio of the lever and the weight at its end. Tests were made at pressures from 20 to 500 pounds per square inch. Cures were timed by a stopwatch from the time pressure was applied in the press at the beginning of the cure of the time pressure was removed at the end of the cure.

CONTROL OF FLOW

It is well known that flow of compounds as molds are closed is often an important factor affecting adhesion. The importance of this wiping action is especially obvious when thermoplastic adhesives are used. Even under other conditions flow may be important.

Minimum flow in the mold is obtained by using an unvulcanized blank having the same diameter as the metal disks. Under this condition, when pressure is applied, flow unavoidably occurs around the edge of the metal disks, and the contents of the mold change in shape from that shown in Figure 4*A* to that in *B*. This flow will be called "overflow." Since in adhesion the wiping action is mainly a surface consideration, flow is expressed in this paper as a ratio of areas. Figure 4*C* is intended to illustrate this point by showing the overflow as an equivalent extension of the diameter of the vulcanizate. If the area of the equivalent disk is compared to the nominal area of test piece, the excess is 25 per cent in the simple assumed case of Figure 4.

Calculation of the overflow, therefore, may be based on the ratio of the volume of overflow to the volume included between the disks as follows:

$$\text{Per cent overflow} = \frac{V_1 - V_0}{V_0} \times 100 \text{ per cent}$$

where V_0 = volume included between metal disks
= gage of vulcanizate multiplied by area of disks
gage of vulcanizate = gage of test-piece minus combined gage of metal disks
V_1 = volume of vulcanizate = weight of vulcanizate divided by specific gravity
weight of vulcanizate = weight of test-piece minus combined weight of disks

It will be recognized that the percentage of overflow is greater for soft stocks than for hard stocks, greater for high vulcanization pressures than for low pressures, and greater for thin test-pieces than for thick ones.

Minimum flow conditions in the mold to produce a test-specimen with a nominal gage of $\frac{1}{8}$ inch are obtained by using a blank having a cross-sectional area of of 2 square inches and a gage of 0.125 inch. By using a blank which has the same volume, greater height, and smaller cross-sectional area, flow in the mold can be increased. In the example of Figure 5 a blank, 0.5 inch high and 0.80 inch in diameter, covers only 25 per cent of the area of the metal disks when it is placed in the mold. When pressure is applied, flow occurs over 75 per cent of the area of the disks, followed by some overflow. The total per cent flow is given by the sum of the per cent of original area not covered by the disk and the per cent overflow.

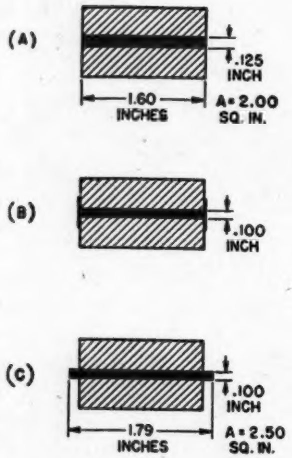

FIG. 4.—Conditions for minimum flow.

(*a*) Section through test-specimen before application of pressure, showing original dimensions of blank.

(*b*) Section through vulcanized test-specimen, showing overflow and final gage of vulcanizate.

(*c*) Equivalent section for vulcanized test-specimen showing over flow as excess in area. Per cent overflow=

$$\frac{2.50-2.00}{2.00}\times 100=25\%$$

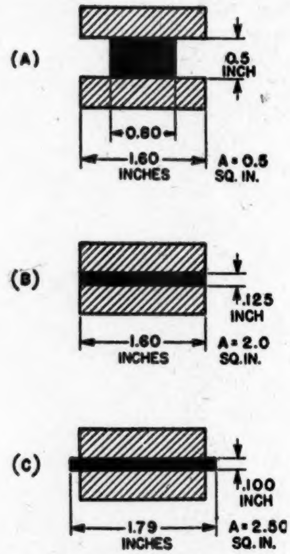

FIG. 5.—Conditions for maximum flow.

(*a*) Section through test-specimen before application of pressure, showing original dimensions of blank.

(*b*) Test-specimen, showing increased diameter of blank due to application of pressure, but before occurrence of overflow: Per cent flow=

$$\frac{2.00-0.50}{2.00}\times 100=75\%$$

(*c*) Equivalent section through test-specimen after the occurrence of overflow: Per cent overflow=

$$\frac{2.50-2.00}{2.00}\times 100=25\%$$

Total flow=75+25=100%

LOAD-ELONGATION CURVE

Test-pieces were evaluated by tensile tests on an autographically recording Olsen Universal Testing Machine with a capacity of 2000 pounds; the capacity relative to the test pieces was thus 1000 pounds per square inch. All test-specimens were pulled apart at a rate of 1 inch per minute.

Failure occurs in three ways:

(1) Complete failure of the bond, permitting the test-piece to pull apart completely by stripping the stock away from the surface of the metal. When adhesion is obtained by the use of cements, failure may occur between the adhesive and the metal or between the adhesive and the stock. When two or three layers of cement are used, failure may occur between the layers.

(2) Tearing of the stock, leaving a substantial layer of Neoprene on the surface of the metal.

(3) A combination of (1) and (2), leaving portions or even only spots of the metal covered with vulcanizate.

The shape of the load-elongation curve indicates to a certain extent the type of failure that has taken place. For example, Figure 6 indicates complete failure

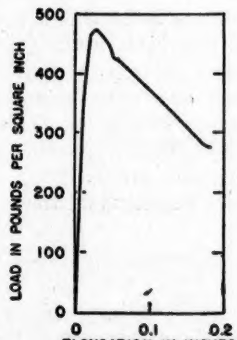

FIG. 6.—Load-elongation curve, showing coincidence of yield point and ultimate strength.

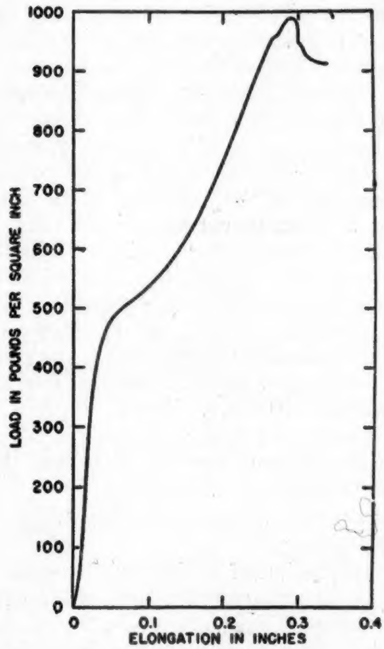

FIG. 7.—Load-elongation curve characteristic of failure by tearing of vulcanizate.

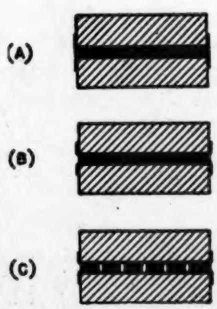

FIG. 8.—Changes in shape and structure of test-specimen during elongation.

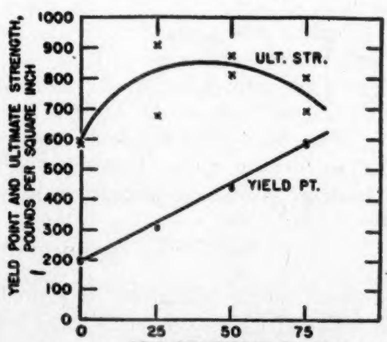

FIG. 9.—Variation of ultimate strength and yield point with amount of semireinforcing black in stock.

Abscissae are expressed in parts by weight in a compound containing 100 parts of Neoprene.

of the bond, as described under type 1. This shows adhesion of Neoprene compound No. 1333N-86 to an adequately cleaned brass surface. The stress-strain curve is practically a straight line to a load of 300 pounds per square inch. Above 300 pounds per square inch the line curves slightly towards the horizontal and at 472 pounds reaches its ultimate strength. Bonds of this type in actual service would give no previous warning of failure but would let go suddenly.

Failure of type 2 is illustrated in Figure 7. Here the loads elongation curve is practically a straight line to 300 pounds per square inch. Above 300 pounds per square inch the line leans to the horizontal and in the load range between 470 to 500 pounds per square inch shows a definite yield. Observation of many test-pieces leads to the conclusion that the yield point is the result of internal rupture of the vulcanizate. This is illustrated in Figure 8. *A* shows a section through a test-piece before stretching. *B* shows a test piece approaching the yield point but before rupture. *C* shows a test-piece after rupture has commenced. Lateral tensile stresses in the vulcanizate in *B* develop as the metal disks are pulled apart. Rupture relieves these lateral forces and causes the yield on the load-elongation curve. Beyond rupture further direct pull is possible and is shown as the rise of the stress-strain curve to the ultimate, strength in Figure 7. When the ultimate strength is reached, the stock tears laterally and the strength of the test-piece is destroyed.

Failures of type 3 cause the load-elongation curves to assume an almost infinite variety of shapes.

In application of engineering materials a permissible working load would be specified as some portion of the yield point. In service in a structure if the yield point were exceeded, the over-stressed part might be functionally impaired by internal rupture, but it would remain structurally intact if the ultimate strength were not exceeded. Therefore, if the ultimate strength is well above the yield point, such a structure would be intrinsically safer than it would be if the yield point and the ultimate strength coincided.

The value obtained for the yield point depends not only on the gage of the stock, as will be shown later, but also on the modulus of the stock. Usually a stock with high modulus will show a high yield point and a stock with low modulus will show a low yield point. Low tear resistance will affect values of the ultimate strength. Figure 9 shows the effect of various amounts of semireinforcing black on the yield point and ultimate strength of a Neoprene Type E compound (similar to compound No. 1333N-86) adhered to brass. The yield point and ultimate strength will also be lowered by poor dispersion or porosity.

EFFECT OF GAGE

Test-pieces are not vulcanized to a predetermined gage in the present apparatus. A series of tests to determine the influence of gage on numerical results is presented graphically in Figure 10. It is impossible to select a significant value for the yield point of thick test-pieces. The difficulty is apparent from examination of Figure 11. Test-piece 156A with a gage of 0.481 inch shows no sharp yield point; test-piece 80 with the same vulcanizate but with a gage of 0.115 inch shows evidence of yield at about 480 pounds per square inch. Since these data make it evident that gage is an important factor, the tables include the gage of the vulcanizate. On the other hand, although values for ultimate strength appear to be definitely higher as the gage is decreased below 0.100 inch, it does not appear that there is any very pronounced effect for gages above this figure.

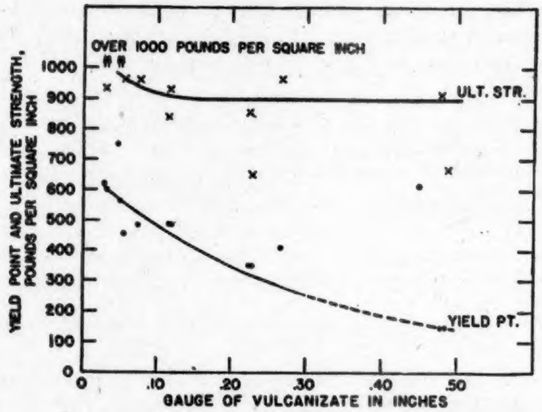

FIG. 10.—Variation of ultimate strength and yield point with gage of vulcanizate.

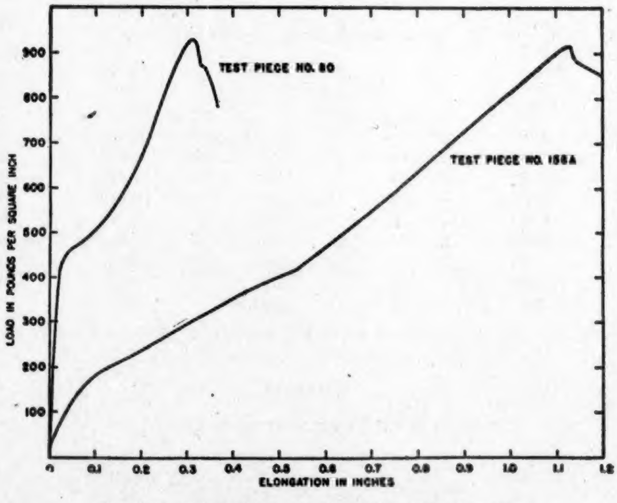

FIG. 11.—Effect of gage on load-elongation curves.

ADHESION TO BRASS AND BRASS PLATE

Adhesion to brass plate is more important commercially than adhesion to brass, but probably is not quite so capable of duplication. For that reason it was thought advisable to use brass of a definite composition in the study of factors relating to compounds and vulcanization. The following composition was adopted:

Lead	1.89
Copper	64.20
Iron	0.14
Zinc (by difference)	33.77
	100.00

This brass is representative of a large group of commercial brasses roughly designated as 70-30 but containing up to 2 per cent or more of lead as a necessary

ingredient for rolling extruding, and machining. It is likely that brass similar to that described above is widely used for inserts in molded rubber goods.

The following compound (1333N-86) was used for most of this work on adhesion to brass:

Neoprene Type E	100
Extra light calcined magnesia	10
FF wood rosin	5
Semireinforcing carbon black [a]	50
Cottonseed oil	5
Neozone D	2
Sulfur	1
Zinc oxide	10

[a] The semireinforcing black used in this and in other recipes in this paper was Gastex.

Table I shows results obtained from test-pieces cured various lengths of time. Satisfactory adhesion is obtained at the conventional cure of 40 minutes at

TABLE I

EFFECT OF LENGTH OF CURE [a]

Test No.	Length of cure (min.)	Flow (%)	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
36	20	10	420	800	0.110
37	20	21	400	400	0.102
34	40	14	500	1000	0.106
35	40	19	500	970	0.100
38	80	25	520	1000	0.098
39	80	10	540	1000	0.102
40	120	23	530	920	0.094
41	120	7	540	895	0.104

[a] Curing temperature, 307° F; compound 1333N-86; pressure, 25 pounds per square inch.

TABLE II

EFFECT OF TEMPERATURE OF CURE [a]

Test No.	Cure (min./° F)	Flow (%)	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
34	40/307	14	500	1000	0.106
35	40/307	19	500	970	0.100
124	180/274	25	520	940	0.103
124A	180/274	18	500	920	0.105

[a] Compound 1333N-86; pressure, 250 pounds per square inch.

307° F and also for longer cures. It will be noticed that the yield point increases progressively with cure. On the other hand, the ultimate strength is low for both the 20-minute and the 120-minute cures. It is evident that undercures must be avoided but that overcure is not a critical factor. Table II compares cures at two temperatures.

Table II shows that there is no appreciable difference between adhesion obtained by equivalent vulcanization at 274° or 307° F if the pressure on the compound is adequate. Data on the effects of pressure are given in Table III.

The load-elongation curves obtained from specimens vulcanized under a pressure of 20 pounds per square inch at 307° F showed no definite yield point but low tensile strength (Table III). Examination of the broken test-pieces revealed coarse porosity. Porosity was also evident for pressures of 50 and even 75 pounds per square inch. There is no apparent difference between cures under pressures of 100 and 500 pounds per square inch. Test-piece 230, vulcanized under a pressure of 20 pounds per square inch but at a temperature of 274° instead of 307° F, developed very good physical characteristics, without porosity. The importance of considering both pressure and temperature as factors in the occurrence of porosity is clearly shown. In factory production, especially if the mold is complicated, it is probable that the pressure will not be equal in all parts of the mold. If the stock has a tendency to blow or if air has been trapped in the mold, the time required for escape of gases by diffusion is a factor in the occurrence of porosity. For that reason it is probable that longer cures at lower temperatures have advantages over short cures at high temperatures; the tendency under extreme flow conditions is to produce a more solid vulcanizate.

Table III

Effect of Pressure during Cure [a]

Test No.	Pressure (Lbs./per sq. in.)	Cure (Min./° F)	Flow (%)	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
65	20	40/307	1	—	460	0.119
112	20	40/307	3	—	540	0.118
113	50	40/307	9	470	630	0.106
113A	50	40/307	9	470	630	0.108
114	75	40/307	8	440	530	0.115
114A	75	40/307	9	440	850	0.114
115	100	40/307	11	480	910	0.101
115A	100	40/307	11	480	890	0.106
116	500	40/307	11	480	900	0.105
116A	500	40/307	10	470	830	0.111
230	20	120/274	3	450	869	0.111

[a] Cure, 40 minutes at 307° F; compound 1333N-86.

Table IV

Effect of Surface Condition of Brass [a]

Test No.	Treatment of brass	Flow %	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
177	Surface of metal rubbed with finger.......	12	470	669	0.115
178	Surface of metal coated with machine oil..	11	380	393	0.125
180	Disks allowed to stand for 24 hr. after cleaning	12	470	1000+	0.110
181	Disks freshly cleaned before vulcanization.	13	490	1000+	0.107

[a] Cure, 40 minutes at 307° F; pressure, 250 pounds per square inch; compound 1333 N-86.

For the tests of Table IV, the brass surfaces were treated differently. There is no practical difference between the adhesion obtained to freshly polished brass and to brass which has been allowed to stand on the work bench for 24 hours after polishing. Intentional contamination of the surface in one case by rubbing the center of the polished brass with a finger and in the other case by dipping

the brass disk in machine oil have resulted in marked decreases in the quality of the adhesion. Test pieces 180 and 181 in Table IV did not fail. Test pieces 177 and 178 failed by separation of the stock from the brass over a large portion of the area. Usually, properly prepared test-pieces fail by tearing of the stock midway between the metal disks.

The necessity of sulfur in the Neoprene compound was established by comparing results obtained with compounds 1333N-86 and -105. Data are given in Table V.

	1333N-86	1333N-105
Neoprene Type E	100	100
Extra light calcined magnesia	10	10
FF wood rosin	5	5
Semireinforcing carbon black	50	50
Cottonseed oil	5	5
Neozone D	2	2
Sulfur	1	—
Zinc oxide	10	10

Table V

Effect of Sulfur[a]

Test No.	Compound	Flow (%)	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
34	1333N-86	14	500	1000+	0.106
35	1333N-86	19	500	970	0.100
135	1333N-105	14	—	243	0.121
135A	1333N-105	21	—	243	0.113

[a] Cure, 40 minutes at 307° F; pressure 250 pounds per square inch.

Table VI

Effect of High Flow[a]

Test No.	Flow (%)	Pressure (Lbs. per square inch)	Yield point (Lbs. per square inch)	Ultimate strength (Lbs. per square inch)	Gage (inch)
117	87	250	440	665	0.115
117A	86	250	450	775	0.112
99	62	250	460	752	0.122
100	76	250	480	900	0.115
134	84	100	450	950	0.123
134A	84	100	Porous	590	0.115

[a] Cure, 40 minutes at 307° F; compound 1333N-86.

Test-pieces vulcanized with a minimum of flow are not essentially better than those with greater flow. The lowest figure obtained for the ultimate strength in Table VI was 665 pounds per square inch with a total flow of 87 per cent across the surface of the disks. Although this represented far from perfect adhesion, the product would still be commercially useful and probably for most uses entirely satisfactory.

The difference between test-pieces 134 and 134*A* in Table VI is significant. The fact that porosity developed in one case and not in the other at 100 pounds per square inch indicates that the cure was conducted at the lower limit of pressure for high flow conditions. Therefore flow should be considered jointly

with temperature and pressure as critical variables in the occurrence of porosity and poor physical properties.

Neoprene Type G compounds containing 0.5 to 1 per cent of sulfur on the Neoprene will adhere to brass as well as comparable Type E compounds. In the interest of brevity, no supporting data are given here, but ultimate strengths above 1000 pounds per square inch have been obtained. Excellent adhesion to commercial brass plate has been obtained with both Types E and G.

ADHESION TO METALS BY CHLORINATED RUBBER

Chlorinated rubber as an adhesive for Neoprene has been developed to a high degree of perfection[1]. When properly used, it will provide adhesion between

TABLE VII

EFFECT OF METHOD OF APPLICATION [a]

Test No.	Flow (%)	Method of application [b]	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
55	18	A	450	980	0.094
55B	22	A	450	1000+	0.105
73	20	B	480	960	0.096
73A	24	B	480	990	0.096
126	87	C	480	780	0.111
126A	88	C	470	630	0.112
188	13	D	490	680	0.106
188A	18	D	490	955	0.106

[a] Cure, 40 minutes at 307° F; compound 1333N-86; pressure, 250 pounds per square inch.

[b] A=one coat of chlorinated rubber cement applied to metal, one coat to stock blank, and each air-dried 3 minutes.

B=two coats of chlorinated rubber cement applied to metal, and each air-dried 3 minutes; also, surface of stock blank rendered tacky by brushing with benzene.

C=one coat of chlorinated rubber cement applied to metal and air-dried 3 minutes.

D=one coat of chlorinated rubber cement on metal, air-dried 2 hours, followed by one coat of cement of compound 1333N-86, air-dried 10 minutes.

TABLE VIII

EFFECT OF SULFUR [a]

Compound No.	Test	Sulfur content (parts)	Flow (%)	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
1333N-105	193	0	12	420	510	0.105
1333N- 86	188A	1	13	490	955	0.106
1333N-106	194A	2	14	550	999	0.102
1333N-107	195	3	16	570	1000+	0.110
1333N-108	198	5	16	600	893	0.106
1333N- 86	199A	1	88	470	780	0.111

[a] Cure, 40 minutes at 307° F; pressure, 250 pounds per square inch.

Neoprene and metal which is essentially on a par with adhesion to brass. Under some conditions the attainment of strong adhesion is critical, and careful examination of various methods of using the cement has been undertaken.

In Table VII results obtained with various methods of application are given for adhesion between Neoprene compound 1333N-86 and cold-rolled steel. The cement used was a 20 per cent solution by weight of chlorinated rubber in benzene. (Tornesit, 20 centipoises was used throughout the work reported in this paper.)

In spite of the appreciable difference in the ultimate strength obtained for test-specimens 188 and 188A in Table VII, it is believed that method D would be most likely to prove commercially successful. Advantageous modification of chlorinated rubber cements by the addition of Neoprene will be discussed later.

Sulfur is necessary in a Neoprene compound to obtain maximum adhesion to metal by the use of chlorinated rubber, as representative data in Table VIII show. From data now on hand, it appears that at least one per cent of sulfur based on the Neoprene content is desirable, but that there is no justification for more than 3 per cent. The cement was applied by method D described in Table VII. The following base compound 1333N-x was used:

Neoprene Type E	100
Extra light calcined magnesia	10
FF wood rosin	5
Semireinforcing black	50
Cottonseed oil	5
Neozone D	2
Zinc oxide	10
Sulfur	As indicated in Table VIII

Comparison of tests 199A and 188A in Table VIII shows that adverse flow conditions can be expected to reduce but may not seriously impair adhesion. Failure of test-specimen 199A occurred principally between the compound and the chlorinated rubber film, as Figure 12 shows. It can be seen, however, that the film

FIG. 12.—Uniformity of a chlorinated rubber film after being subjected to severe flow conditions.

on the left-hand disk is intact and uniform. Under similar conditions Thermoprene (adhesion with rubber isomers[1]), which is known to be thermoplastic, was wiped badly by 78 per cent flow of a rubber compound at 274° F as Figure 13 shows. The lightly colored areas on the right-hand disk show where the adhesive has been wiped almost clean from the metal. Circular ridges caused in the film by flow are also apparent.

Experiments were conducted with cements containing both chlorinated rubber and Neoprene. The cements consisted of a 20 per cent solution by weight in benzene of chlorinated rubber and Neoprene compound 1333N-86 in the proportions indicated in Table IX. In each case one coat of the chlorinated rubber-Neoprene cement was applied to the metal and allowed to air dry for 2 hours, followed by one coat of a 20 per cent cement of compound 1333N-86 which was allowed to air dry for 10 minutes.

Dry films of chlorinated rubber are hard and brittle. The addition of Neoprene to the cement softens them somewhat and imparts a desirable tough-

ness which should be especially advantageous when the metal surface to which Neoprene is adhered is not entirely rigid. For most production conditions, combination cements of Neoprene and chlorinated rubber appear most useful. The optimum ratio of chlorinated rubber to Neoprene, based on examination of many adhesive films both before and after vulcanization, as well as on the data of Table IX, appears to be 10 to 2.

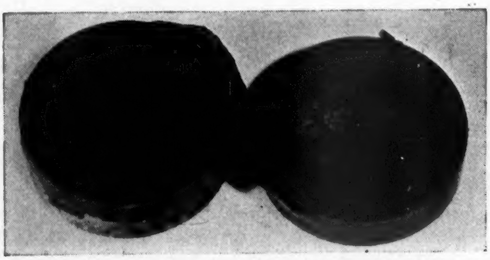

FIG. 13.—Flow of thermoprene resulting from extreme flow conditions.

Experimental results not reported in this paper show that Neoprene may be adhered with apparently equal success to steel, copper, aluminum and 18-8 stainless steel by the use of chlorinated rubber cement.

In concluding this section of the paper, data are given on tests of Neoprene-coated steel panels at 28° and 100° C (82.4° and 212° F). Test panels, 1×4 inches, were made in such a way that coating could be stripped off in a hot tensile-testing machine as follows:

TABLE IX

EFFECT OF CHLORINATED RUBBER [a]

Test No.	Chlorinated rubber/neoprene ratio	Flow (%)	Yield point (Lbs. per sq. in.)	Ultimate strength (Lbs. per sq. in.)	Gage (inch)
188A	10/0	13	490	955	0.106
225A	10/1	17	430	976	0.126
226	10/2	13	430	965	0.135
227	10/4	15	420	785	0.130
228	10/6	13	420	738	0.133

[a] Cure, 40 minutes at 307° F; pressure, 250 pounds per square inch; compound 1333N-86.

Test No.	Compound	Method of preparation
1, 2,	1333N-86	One coat of chlorinated rubber cement applied on steel, allowed to dry for 2 hr. One coat of stock cement applied over this and allowed to dry 15 min. Compounds applied and cured 40 min. at 307° F in water.
3, 4	1333N-86	One coat of chlorinated rubber cement applied on steel, allowed to dry for 2 hr. Stock surface washed with benzene and rolled into place on Tornesit before benzene had completely dried; cured 180 minutes at 228° F in water.
5, 6	1333N-86	Same as 1 and 2, but cured 180 minutes at 228° F.

The results in the following table indicate mechanical durability of chlorinated rubber adhesion at elevated temperatures and the feasibility of wider utilization of Neoprene linings of metal equipment for industrial uses:

Test No.	Temp., ° C.	Lb. pull per linear in., stock tore in each case
1	28	40
3		41
5		55
2	100	12-15
4		10-20
6		25

SUMMARY

The modifications of the A. S. T. M. adhesion procedure which have been introduced for the purposes of this paper have contributed an understanding of the influences of flow and pressure on the quality and strength of Neoprene-to-metal adhesion. Interpretation of results is facilitated by consideration of the yield point on the load-elongation curve in a type of internal failure which can be observed only by the use of relatively thin vulcanizates in the test-piece. It is expected, however, that the value of the ultimate strength in most cases would prove to be about the same, regardless of whether the gage of vulcanizate is $\frac{1}{8}$ or $\frac{1}{2}$ inch. As Figure 10 shows, the value of the ultimate strength has proved to be the same between these two dimensions for one compound adhered to brass.

The two factors, aside from freshness of the compound, which seem to be of outstanding importance in production of parts requiring adhesion of Neoprene to brass are, first, the proper handling of the brass surfaces and, secondly, the proper control of trapped air and porosity. Cleanliness from an adhesion standpoint seems to depend more on contamination of the surface by oil and other dirt than on oxidation due to standing under ordinary atmospheric conditions up to 24 hours. Industrially this point can hardly be overemphasized. With regard to the second point, flow in a mold may produce areas where the pressure is relatively low. Because of the low pressure, porosity can develop, especially since flow increases the likelihood of porosity at a given pressure. The determining factor, therefore, appears to be not the wiping of the surface of the metal by the stock, but the concomitant development of porosity at the interface between the metal and the stock. In addition to its effect on porosity, flow enters in through its effect on the grain of the compound. This point has been obvious from the type of breaks obtained in several cases but is not easily represented numerically.

Cements of chlorinated rubber modified by the incorporation of the proper amount of Neoprene appear to be applicable to a wide variety of industrial uses. The best adhesion obtainable by this method is comparable to the best adhesion to brass or to brass plate. Chlorinated rubber possesses the additional virtue of remaining hard at temperatures up to the decomposition point of about 155° C in contrast to many other adhesives which are thermoplastic.

REFERENCES

[1] Geer, W. C. (to B. F. Goodrich Co.), U. S. Patent 1,744,880 (Jan. 28, 1930).
[2] Habgood, *Trans. Inst. Rubber Ind.* **13**, 136 (1937); Habgood, B. J. and Imperial Chemical Industries, Ltd., Brit. Patent 493,139 (Oct. 3, 1938).

THE QUANTITATIVE DETERMINATION OF ZINC IN TRANSPARENT RUBBER ARTICLES *

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The method to be described is particularly suitable for the quantitative determination of zinc, present in the form of zinc oxide or of zinc salts, in transparent rubber articles. Rubber articles of this type contain very small quantities of zinc compared with the quantities present in non-transparent rubber articles, in fact the lower limit is only 0.05 per cent, *i.e.*, only about one-hundredth as much as the normal content.

The analytic determination of the zinc content when present in such extremely low percentages as this is extremely difficult by ordinary methods, and even with higher but nevertheless small percentages of zinc, the use of relatively large quantities of material is necessary and the analytical results are often far from precise.

The ordinary method of incineration in a porcelain crucible does not lend itself to the isolation of small quantities of zinc because the latter is easily fixed by the silica of the crucible. On the other hand incineration in a platinum crucible is not suitable because of the tendency of this metal to form a carbide in contact with the carbonaceous substances in the rubber.

The novel feature of the method of analysis to be described is the procedure for obtaining a solution of the inorganic substances in the rubber. This involves destruction of the rubber by concentrated sulfuric acid and subsequent oxidation of the organic residue by concentrated nitric acid.

This gives a solution of the zinc in the form of sulfate. It is then isolated as zinc sulfide and is redissolved and determined volumetrically by the already known method of precipitation with a standard solution of potassium ferrocyanide.

The most suitable concentration, acidity and temperature to give precise results by this procedure for low percentages of zinc in rubber were established.

PROCEDURE

Cut two grams of the rubber to be analyzed (5 grams if the percentage of zinc is less than 0.1) into small pieces, place in a round-bottom flask of 500 cc. capacity made of refractory glass and having a long neck, add 20 cc. of a mixture of 3 parts by volume of concentrated sulfuric acid and 2 parts of fuming sulfuric acid, close the flask with a pointed glass bulb, heat the contents at first moderately and then more strongly so that the liquid boils steadily.

When the rubber is completely dissolved and the liquid is red-brown, add 1 cc. of fuming nitric acid and heat for several hours, as before. If the liquid is not clear and colorless when cold†, add a few drops of fuming nitric acid, heat two or three hours longer, and repeat the operation until the tarry and carbon-

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† If the rubber contains compounding ingredients, the solution may be turbid and colored or may deposit an insoluble residue. In any case, the oxidation is continued to the point where the tarry substances are oxidized and the solution remains unaltered when more nitric acid is added.

aceous substances are completely oxidized (usually the first addition of nitric acid is sufficient).

Transfer the liquid to a broad glass capsule, rinse the flask repeatedly (adding the wash waters to the liquid already in the beaker), and evaporate the solution to dryness by gentle heating until white fumes are no longer evolved. Spattering must be avoided, and it is well to add glass beads.

To the dry residue add 30 cc. of dilute (1:3) hydrochloric acid, boil, allow to stand on a steam bath for one-half hour, neutralize with ammonium hydroxide, heat to 70-80° C, add excess ammonium hydroxide (approximately 5 cc.), carry to the boiling point, again allow to stand on a steam bath for one-half hour, filter (washing thoroughly the beaker and the precipitate), allow the filtered liquid to stand for 12-24 hours, add a few drops of ammonium hydroxide, heat, filter off any precipitate which may still form, boil the filtrate for 5 minutes in a glass beaker of 250 cc. capacity to expell excess ammonia (no precipitate should be formed any longer), carry to the boiling point, add dropwise freshly prepared white ammonium sulfide solution until no more precipitate is formed, allow to stand for one-half hour on a steam bath, filter, and wash the residue three times with water containing a few drops of ammonium sulfide.

Onto the still moist filter pour, in three portions, 20 cc. of boiling dilute (1:2) hydrochloric acid, wash with 20 cc. of boiling water to dissolve completely the precipitate of zinc sulfide, boil the filter to eliminate hydrogen sulfide, add ammonium hydroxide until the solution is slightly alkaline to litmus, add 0.5 cc. of concentrated (37%) hydrochloride acid, dilute to 100 cc. with water and heat to 90° C.

Titrate the resulting hot solution with standard potassium ferrocyanide solution; the latter is added dropwise from a burette to the solution to be titrated, which is kept agitated with a glass rod, until a drop of the liquid, tested on filter paper previously wetted with a 5 per cent uranyl nitrate solution, does not leave a brown stain.

The brown color at the neutral point appears slowly, and it is therefore necessary, in the test with the indicator, to proceed slowly and with great care, and later to add at intervals one or two more drops of liquid on the same spot. This special technique is of great importance for obtaining precise results.

Preliminary tests will serve as a ready means of gaining experience in the manipulations involved in the procedure and in avoiding the addition of an excess of reagent.

By knowing the volume of potassium ferrocyanide solution used and also the titer of this solution in terms of zinc, the zinc content of the rubber sample can be calculated:

$$\%\ Zn = \frac{(a-b)T}{P} \times 100$$

where

a = no. of cc. of $K_4Fe(CN)_6$ solution used.

b = no. of cc. of $K_4Fe(CN)_6$ solution used for a blank test made under the same conditions (*loc. cit.*).

T = titer of the $K_4Fe(CN)_6$ solution

p = no. of grams of rubber sample

PREPARATION OF THE POTASSIUM FERROCYANIDE SOLUTION

The standard potassium ferrocyanide solution is prepared by dissolving 21.12 grams of pure potassium ferrocyanide in distilled water and diluting to one liter.

DETERMINATION OF THE TITER IN ZINC OF THE POTASSIUM FERROCYANIDE SOLUTION

The titer of the potassium ferrocyanide solution, prepared in the way described above, is determined by titration with a solution having a known zinc content.

Dissolve approximately 1 gram of pure granular zinc (arsenic-free) in 10 cc. of concentrated hydrochloric acid, dilute with 20 cc. of distilled water, transfer to a graduated flask and dilute to 200 cc.

Transfer 5 cc. of this solution to a 250-cc. beaker, add 20 cc. of dilute (1:2) hydrochloric acid, add ammonium hydroxide until slightly alkaline to litmus, add 0.5 cc. of concentrated (37 cc.) hydrochloric acid, dilute with water to 100 cc., heat to 90° C, and titrate with standardized potassium ferrocyanide solution, using 5% uranyl nitrate solution as indicator, and following the same procedure used in determining zinc in rubber as described above.

A blank test is then made, again operating in the same way, *i.e.*, with the same quantities of reagents and water, but substituting 5 cc. of distilled water for the 5 cc. of zinc chloride solution.

All titrations, including that of the solution obtained from the rubber sample, that of the zinc chloride solution of known titer and that in the blank test, should be made under identical conditions of temperature, concentration and acidity.

The titer of the potassium ferrocyanide solution in terms of zinc, *i.e.*, the number of grams of zinc corresponding to 1 cc., is as follows:

$$T = \frac{P}{40(A-B)}$$

where

P = no. of grams of zinc used
A = no. of cc. of $K_4Fe(CN)_6$ solution used for the $ZnCl_2$ solution
B = no. of cc. of $K_4Fe(CN)_6$ solution used in the blank test.

The titer of the potassium ferrocyanide solution is independent, at least within certain limits, of the concentration of zinc in the solution to be titrated.

The following table gives the results of determinations carried out with 5-cc., 2.5-cc. and 1-cc. portions of a solution of 1.0224 gram of zinc in 200 cc., and also with a blank.

Cc. of $ZnCl_2$ solution	Zn in grams	Cc. of $K_4Fe(CN)_6$ solution (A)	Cc. of $K_4Fe(CN)_6$ solution (A-B)	Corresponding percentage of Zn in rubber
5	0.02556	5.45	5.20	1.278
2.5	0.1278	2.85	2.60	0.639
1	0.00511	1.30	1.05	0.255
0.5	0.00255	0.75	0.50	0.127
0	0	0.25	0	0

The fourth column gives the number of cc. of potassium ferrocyanide solution actually used to precipitate the corresponding quantity of zinc from the solution

of zinc chloride, *i.e.*, the values in the third column minus the corresponding value in the blank test. This value of the blank test is the last value in the third column.

Disregarding negligible differences, these values are proportional to the zinc content, and this proves that the titer of the potassium ferrocyanide solution is constant for various quantities of zinc.

This fact is particularly important in the determination of the percentages of zinc in rubber articles in which the zinc contents differ.

The fifth column gives the percentages of zinc which should be present in the rubber mixture (assuming a 2-gram sample as specified in the procedure) based on the consumption of the corresponding quantities of standard potassium ferrocyanide solution. It is evident that, within the limits of 1.2 and 0.12 per cent of zinc in rubber, the magnitude of the errors involved in this method of titration does not depend on the percentage of zinc in the rubber.

Finally determinations were carried out with rubber samples containing known percentages of zinc oxide, *viz.*, 0.5, 0.25 and 0.10 per cent, respectively, and weighed accurately. Zinc was also determined by the usual method of incineration in a porcelain crucible and precipitation by zinc pyrophosphate. The results obtained by the two methods are recorded in the following table.

Quantities of rubber sample analyzed	
New method	2 grams
Pyrophosphate method	10 grams

	Percentage of ZnO by analysis	
Actual percentage of ZnO in rubber	New method	Pyrophosphate method
0.5	0.490	0.459
0.25	0.245	0.192
0.10	0.101	0.072

A comparison of these data shows that, with such low percentages of zinc oxide, the pyrophosphate method gives abnormally low results, whereas the new method gives unusually precise results. The precise results obtained by the new method are particularly noteworthy when it is further considered that the zinc oxide used contained 98.5 per cent of actual zinc oxide.

In addition to this degree of precision, it must be remembered that the determinations as pyrophosphate were made with 10 grams of rubber sample, whereas the new method required only 2 grams. Nevertheless, as has already been noted, when the percentage of zinc is less than 0.10 per cent, it is advisable, even with the new method, to use 5 grams instead of 2 grams of rubber sample if the material is available. With this larger quantity the precision is greater.

RÉSUMÉ

An especially precise method for determining small percentages of zinc in rubber is described. This method is based on dissolution of the rubber sample by concentrated sulfuric acid and concentrated nitric acid and subsequent volumetric determination of zinc by precipitation by potassium ferrocyanide solution.

The most suitable conditions of concentration, acidity and temperature to obtain precise results by this method with small quantities of zinc have been established.